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Lars Onsager (1903–1976)

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By 1933 the Depression had taken such a toll on the finances of Brown University that its chemistry department, in anguish, was forced to terminate the appointment of a brilliant young research professor. In what he described as his most significant professional action, Herbert Harned then persuaded Lars Onsager, for he was the unemployed genius, to accept a Sterling Fellowship at Yale. Upon Lars' arrival in New Haven there was one slight, awkward development; the fellowship was a postdoctoral appointment and Lars had not bothered to take a Ph.D. Harned's solution was a Yale Ph.D. To satisfy the dissertation requirement, Lars swiftly produced from his files a manuscript titled, "Solutions of the Mathieu Equation of Period 4π and Certain Related Functions." Because it was incomprehensible to Yale's chemists and beyond the critical competence of its physicists, Harned carried it to Einar Hille, a well known mathematical analyst. Hille judged the work superb and is said to have suggested a Ph.D. in mathematics. Stronger wills prevailed. Lars took his degree in chemistry and slipped the manuscript back into his files unpublished. Harned found it amusing, if somewhat tedious, that a young man with a spectacular record of accomplishment and unbounded intellectual promise should be presented this hurdle even if it could be cleared with a simple step by a giant. Harned never ceased to wonder what combination of gifts, influences, and good fortune produced such an extraordinary person. We can be reasonably certain that it was not altogether chance.

The son born to Erling and Ingrid Onsager on 27 November 1903 was named Lars. Erling was a lawyer and, if we are to judge from the family's comfortable circumstances, a successful one. Life with the Onsagers meant being surrounded by books and art (Erling was an avid collector of the works of Munçh). It involved leisure and travel for an inquisitive child and, most importantly, it meant having a mother clever enough to recognize an

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even more clever son, whose dazzling facility in mathematics should be nurtured. These familial influences did not guarantee that Lars would emerge as a thoughtful, gracious man of taste, at ease with languages and literature, who might have moved into history or mathematics with as much assurance as into science, but it would be rash to assume these influences were without effect.

Onsager's parents also provided him with a fortunate genetic heritage. He was a big, powerful fellow—a member of championship four-oared crew at Zürich, someone known to ski from Hamden to the Sterling Chemistry Lab during very heavy snowfalls. He matched robust physical attributes with a marvelous temperament; he was calm as silk and had a will as resilient as bronze. As he entered the Norwegian Institute of Technology, his abilities, spirit, and staying power must have marked him for the thoroughbred he was.

We only know a bit about his five years as a chemical engineering student. He enjoyed that experience and had great respect and affection for his teachers, who obviously encouraged his interest in mathematics and his passion for fact. Much has been said of Lars' memory. I shall agree that it was awesome, but it differed in one way from almost any other I have encountered. Lars seemed to store away not just facts but patterns of facts. As a consequence, for Lars a new bit of information either fit the pattern or immediately became a puzzle, and Lars enjoyed solving puzzles. His experience in engineering is barely perceptible in some of his work, on turbulence for example, but there is no question about engineering influence on his early work on the use of diffusion for the separation of isotopes. Late in his career he chaired for a number of years an A.E.C. committee whose work resulted in this country's decision to move to centrifugation as a more energy-efficient process for isotope separation.

In adition to practical fields, his studies extended independently to the theoretical developments of the early Twenties. One such development which attracted his attention was due to Peter Debye and a colleague, Erich Hückel. They had developed a theory to account for the variation with concentration of the thermodynamic and transport properties of very dilute electrolyte solutions. The Debye–Hückel estimate of the difference in free energy of an infinitely dilute solution from that at finite (but low) concentration was just the work required to move the ions against coulombic forces to the equilibrium configuration, one in which an ion of given charge was surrounded by an "atmosphere" of oppositely charged ions with a distribution governed by Boltzmann's law. This free energy estimate was in excellent agreement with careful experimental data. However, the theory was not quite as successful in explaining the concentration dependence of the conductance of dilute electrolyte solutions. This theory requires the computation of the change with concentration of the velocity per unit gradient of electric field which an ion of a given type experiences as its motion is impeded, first by the movement of solvent with the "atmosphere" of oppositely charged particle and, second, by the coulombic interaction of that charged ion with the non-equilibrium configuration of the "atmosphere" moving in the opposite direction. Onsager recognized that the Debye model was flawed. With a delicate correction of the model and an elegant mathematical analysis of his revision. Lars produced a workable theory which agreed very well with experiments. Certainly this was quite an achievement for a college student. Of more significance, however, was an episode which led to probably the most important influence in his professional career.

Many people, even those very talented, drift through life in ways that match their skills (and there is much to be said in favor of this). It is the mark of a great teacher that he will point the able in the direction of favorable currents. Peter Debye, in addition to being the foremost physical chemist of his time, was also an inspiring teacher. Onsager, after finishing his engineering degree, made an uninvited visit to Debye's laboratory at the E.T.H. in Zürich. Stories about the first meeting of these two men vary, but all agree that the first complete sentence in that meeting was, "Professor Debye, your theory of electrolytes is incorrect." Debye was persuaded that Lars was right, and advanced the latter's ideas whenever possible. Early in the following year Debye invited Lars (minus a doctorate) to be a research assistant, which post he occupied for two crucial years. During that time Lars published his theory of the limiting law for electrolytes, and Debye brought this work to the attention of the scientific world in his customary, persuasive manner.

Europe in 1928 was a troubled area while in the United States the mood was still buoyant. As it did for so many ambitious Europeans of the time, America must have seemed a land of promise to Lars. For whatever the reasons, he accepted a post at Johns Hopkins University, where the taught the elementary chemistry course. In retrospect, the assignment must be judged incongruous; at the time it seemed to bewildered students to verge on cruelty. With his awesome control of facts, his swiftness, clarity and elegance of thought, and his extraordinary facility in mathematical analysis, Lars was, in a literal sense, no match for freshmen. As a result, and probably with relief all round, Lars was terminated at Hopkins in his first year.

This difficulty in communicating with others was not restricted to freshmen. Lars simply could not appreciate the intellectual limitations of average persons (this included most of his scientific colleagues). Later in his career, the brightest of graduate students were to learn that Lars' course in statistical mechanics could be illuminating, if one attended with prior knowledge of the contents of the stadard monographs, was prepared for non-standard and rapidly changing notation, and was keyed up to listen carefully despite repeated feelings of hopeless inadequacy. The most successful students took the course twice. Lars' papers also posed a problem for speed-readers. Although his writing was exquisite, it has also been described as "spare to the point of being cryptic."

Disregarding Lars' performance as a teacher of freshmen, Charles Krauss, the formidable chairman of the Brown chemistry department, was quick to recognize an opportunity and appointed Onsager as a research instructor. At Brown, Lars returned seriously to the problem which had vexed Lord Kelvin, the symmetry of interactions in coupled flows. Lars had already shown that given ionic fluxes, J_i, in dilute electrolyte solutions were represented by $J_i = \sum_k L_{ik} h_h$, where the h_k's are gradients of the potentials acting on the various ions. He also had shown that the matrix of coefficients L_{ik} was for this case symmetric. In 1929 he published an abstract of a proof that this same symmetry was characteristic of all coupled flows. His recipe, now familiar, is straightforward. If for a set of coupled flows (heats, matter, electricity, etc.), the rate of entropy production is $\dot{S} = \sum_i J_i X_i$ where X_i are the forces conjugate to the flows J_i and the system is close enough to equilibrium so that $J_i = \sum_k L_{ik} X_k$ (i.e., the individual flows can be written linear in the varous forces), then $L_{ik} = L_{ki}$. These equalities are known as the Onsager Reciprocal Relations. This most significant extension of thermodynamics since Gibbs (often called the Fourth Law) led many years later to his Nobel prize, in 1968. In fact, years elapsed before experimentalists recognized the importance of the idea. For example, an investigator interested in flows of ions, solvent, and current through a biological membrane using the Onsager procedure, now knows that to describe the system adequately, it is necessary to set up appropriate experiments to determine the coefficients, L_{ik}. The Onsager Relations make his work much simpler, for only half the off-diagonal matrix elements need be determined. Obviously, the investigator can also monitor the quality of his experiments by an occasional check of the Onsager Relation. In some experiments the L_{ik} can be calculated from first principles; sometimes they can be estimated crudely.

A year following the publication on the Reciprocal Relations, Onsager, together with a brilliant young student, Raymond Fuoss, published a classic paper on irreversible processes in electrolyte solutions which was, among other things, a masterly application of the Onsager principle. The active collaboration of these two men continued for more than 30 years.

Another application occurred to Lars. If a gas is contained within two concentric tubes held at different temperatures, there will be, in steady state, simultaneous flows of heat and mass. An elaboration of his own theory persuaded Lars that, if the gas were composed of two isotopic species, a separation of isotopes would be observed across the thermal gradient and accentuated by gravitational separation along the length of the tubes. Onsager proposed he do this long before the famous experimental work of Clusius and Dickel. Onsager, Furry, and Jones finally published the theory of isotope separation, known to Lars' statistical mechanics students for a number of years.

Lars was in full stride by 1933, when he left Brown for Yale. During the summer of his move to New Haven, Lars met Margarethe Arledter; and after a brief courtship they were married. The Onsagers first settled in Hamden, but moved a bit later to a larger home as their family grew—they had four children: Erling, Inger (Mrs. Kenneth Oldham), Hans, and Christian. This lively, witty, intelligent family was for Lars a continuing source of pleasure, particularly during vacations when the whole group regularly sped to their comfortable farm in Tilton, New Hampshire. At the farm Lars was free to put his large, competent hands on things, and move them around. He could till and dig, cut down some trees and plant others, and sow and harvest. But even in these idyllic surroundings he could not suppress thought, and often some fresh idea would bring him back from the farm to New Haven and the Yale libraries.

Onsager disliked publication of routine material. As a result, in his first twenty years at Yale, he published just over one paper a year, but all the work was marked by originality (often daring), elegance, and a reassuring air of finality. In his first efforts, very soon after taking his new post, Onsager produced a theory for the Wien effect in weak electrolytes. The effect is simple to describe, but difficult to explain in detail. Ohm's law fails for weak electrolytes; at very high fields the conductivity is much higher than the low field value. Lars interpreted this observation as a perturbation of the equilibrium between undissociated molecules and the corresponding ions in solution. Lars reasoned that the rate of dissociation increased in the high field whereas the recombination rate was unaffected. His intricate calculations predicted a linear change in the dissociation constant with varying field (in the high field regions), the slope of such a plot to be independent of weak electrolyte concentration. Precise experimental verification of this theory had to wait until pulse techniques, which were World War II developments, could be employed; a steady application of applied fields was ruled out because the heat generated lowered the solution viscosity masking the effects being studied. In an experiment beautifully planned and executed, Andrew Patterson and John Gledhill at Yale verified the Onsager theory to the letter. But they did something more. At the finish of the pulse, the Patterson–Gledhill procedure allowed one to follow the return of the conductivity to its equilibrium value. Andy and Jack quickly recognized that they were watching the recombination of the excess ions, in fact looking at rates of reactions on a time scale much shorter than had ever before been accessible. Patterson and his colleagues published a few papers on these rate studies, but it remained for Manfred Eigen and his group to generalize the idea. Using all sorts of methods to perturb equilibria, Eigen studied rates of reactions in systems "relaxing" to equilibrium and, for this magnificent contribution, was awarded the Nobel prize.

In 1936 J. G. Kirkwood (later to come to Yale himself) persuaded Lars to publish a paper on the relation of the dielectric constant and dipole moments of liquids. This paper, prepared in a German version while Lars was still at Brown, had been denied publication in the *Physikalische Zeitschrift* by Debye, whose earlier theory on the same subject Onsager had effectively dismantled. By this time Debye might justifiably have wondered when this blonde bruiser was going to pick on someone else, but with his customary sense of balance and his instinct to move the field ahead, Debye once more gracefully accepted his protege's correction.

In the early 1930s Lars became interested in isotope separation by thermal diffusion. Meanwhile at Yale William Watson had become interested in isotope effects in spectroscopy. A successful collaboration with Lars on isotopic separation and identification resulted. Soon after that work was published the United States was at war and Lars, not yet a citizen, did not participate in formal scientific support of the war effort. Watson did, and in due time thermal diffusion as a technique for isotopic separation became a useful procedure in the Manhattan Project.

Although Lars was isolated from the scientific effort supporting the war, he was not idle. Early in that period he tackled and solved one of the great problems in modern physics. He set out to show that the methods of statistical mechanics can account for sharp phase transitions in matter. No analytical proof existed before 1942 that such sharp transitions would occur for arrays of particles which had only finite nearest neighbor interactions. Lars determined, in closed form, the partition function for such a two-dimensional array (the Ising lattice). Knowing the partition function, he was able to get the free energy of the lattice as a function of teperature and establish that the Ising lattice had phase transitions. Moreover, he demonstrated that, near the phase transition, for the infinite crystal the specific heat would vary with the log of the difference between the actual temperature and the temperature of the transition. This latter prediction was verified by William Fairbanks at Duke in a study of the heat capacity of helium through the lambda point. Fairbanks's interest in the problem was not too surprising, for he took his degree at Yale with Cecil Lane in low temperature physics, and Lars was in constant collaboration with that group. Lars published the full elegant paper on the Ising lattice in 1944 and, together with Bruria Kaufman, an even more direct and yet more elegant route to the same majestic conclusion. The work with Kaufman also resulted in an accurate description of the spontaneous magnetization of a two dimensional ferromagnet.

Onsager's interest in low temperature physics led to several other important contributions. First, he showed that for superfluid helium the critical velocity of flow depended on quantized circulation. With the same guiding philosophy he argued that the currents in a superconducting ring were limited by quantum mechanics to values dependent on eigenvalues of the electronic wave function. Onsager argued that if the currents were quantized, so would be magnetic fields produced by superconducting rings. The two low-temperature themes were presented orally at international meetings. Fairbanks had justifiable confidence in Onsager and, this time at Stanford, he produced experimental work that verified the Onsager argument for superconducting rings. Fairbanks persuaded Lars to publish a note on this subject at the time of the publication of experimental results. His general interest in low-temperature physics took Lars, as a Fulbright Scholar, to Cambridge in 1951. While there he pursued a problem that he encountered in Lane's laboratory. For diamagnetic crystals the magnetic moment changed periodically with the strength of an applied magnetic field. Lars was able to account for this deHaas–van Alphen effect, and several years later his theory was quantitatively verified by Shoenberg at the Mond laboratory.

In the Fifties John Kirkwood, a longtime friend and colleague of Lars, was persuaded to come to Yale. Jack had just the qualities needed to create a school of theoretical chemistry, while Lars was very much the individualist. The presence in Sterling Laboratory of Jack's large group of bright, aspiring theorists was for Lars a rewarding arrangement. For the first time in his teaching career he met more than a few students at a time who were committed to theoretical chemistry (almost exclusively to statistical mechanics). They were naturally interested in the things Lars put together in his courses. But it was in the theoretical chemistry seminar that the combination of Jack and Lars was seen to best advantage. Lars was there to gently challenge and make subtle suggestions which Jack was able to interpret and clarify.

During the Sixties Lars also considered the problem of the heat capacity of the surfaces of solids, made several more contributions to the physical chemistry of electrolytes, and began his self-education in the field of neuroscience. But his principal effort in that decade was a long, detailed development of a theory for ice and "doped" ice. It must be recognized as Lars' last great virtuoso performance. With this effort Lars showed the power of kinetic theory applied to a problem for which a more rigorous method was not feasible. Using the known structure of ice, accepting Bjerrum's concept that random rotations of molecules within the ice lattice can produce "faults," Lars, exhibiting considerable cunning, explained the dielectric properties, the electrical conductance, various relaxation effects, and self-diffusion of ions. After developing a plausible model for ice as a semiconductor, he was successful in predicting the behavior of ice "doped" with simple ions other than the proton or the hydroxyl ion. One had the feeling that after this long, arduous, and successful exercise the fires were banked in the engine that drove that marvelous thinking machine.

Increasingly Lars devoted more time to biophysics, in particular the functioning of nerve cell membranes, and to speculation about the origin of life on this planet. As a result a greater fraction of his time was spent in reading, listening, and study than was earlier the case when his research took him into uncharted areas. He seemed to relish the speed at which these fields were developing and at the challenges to thought that these results provided. And so it was with this fresh outlook that, rich in years and accomplishments and honors, Lars approached retirement at Yale in 1972.

It had been assumed that Lars would continue his research at Yale, assuming the responsibility for his own support and that of those few post-doctoral workers whom he might invite to work with him. This was not to be. The University had been stung by an action brought by a professor who objected to being retired for what he thought was just a matter of age. To avoid any appearance of invidious distinctions, the University decided to discourage an emeritus professor from being a "principal investigator" on an externally funded research grant, which was a situation quite different from that of a professor asking to be continued on the University payroll beyond retirement age. The University position was challenged; the challenge failed; Lars was miffed and his colleagues were embittered. After a reasonable time to reconsider the issue had passed, Lars accepted an appointment as Distinguished University Professor in the Center for Theoretical Studies at the University of Miami. More than a year passed before the dust settled at Yale. The University attitude was relaxed in subsequent cases and, finally, Yale's President Kingman Brewster explored the possibility of Lars' return to New Haven. That was not to be.

Lars continued at Miami with just the program he had anticipated for Yale. He had a small, lively group of post-doctoral associates, and seemed to appreciate the variety of work and the quality of the scientists (permanent and visiting) for which that Center is so well known. He also managed about ten publications during his stay at Miami. On occasional trips to and from Tilton, he stopped over in New Haven, and all were impressed by the effect of this mix of climates on Lars' physical appearance. He always seemed bronzed and fit. But Lars had a recurring circulatory ailment which some years earlier had given his family several anxious periods. At the end of September in 1976 he chose to fly back directly to Miami from a meeting in Canada; Gretl—Mrs. Onsager—was still at the farm enjoying the golden time in New Hampshire. On 5 October, Joseph Hubbard, a long time research associate, concerned about Lars' absence from the Institute the previous day, went to the Onsager home. He gained entry and found Lars, apparently the swift victim of the ailment which had threatened him before. The grave of the only man to hold the J. Willard Gibbs chair in chemistry is just a short distance from that of Gibbs himself in the Grove Street Cemetery in the shadow of the Yale Law School.

Each station in life has its own special rewards. To have been a chemist at Yale was to have had Onsager as a colleague. He was by nature so magnificently endowed that he could not fail to stir one. To know Lars was to treasure the civilization of which he was so lustrous a product. I have always felt that Lars was one of the men Debye remembered when he wrote, "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."