

KIRKWOOD MEMORIAL SYMPOSIUM

A summary by John S. Dahler

JOHN Gamble Kirkwood was one of world's most distinguished and versatile scientists. His eminence in the field of statistical physics and chemistry was evidenced by his ingenious theoretical analyses which have played a major role in clarifying our understanding of such subjects as order-disorder phenomena, polymers, liquids, solutions, irreversible thermodynamics, transport phenomena in fluids, the propagation of shocks and detonations, molecular quantum mechanics, liquid helium, and nuclear structure. His theory of electrolytes has been especially valuable in explaining the properties of proteins. Although he frequently dealt with abstract mathematical concepts, many of his ideas had practical applications. For example, he combined electrophoresis with thermal convection to provide an important means for effecting separations of proteins in solution.

In memory of Kirkwood's outstanding scientific accomplishments a three-day symposium of the Physical Chemistry Division of the American Chemical Society was held in conjunction with the Society's 138th national meeting. These sessions took place at the New Yorker Hotel on September 12, 13, and 14, 1960. Among the twenty-odd papers included in the program were representatives of a variety of topics with which the name of Kirkwood has come to be intimately associated. The participants themselves could with few exceptions be classified either as Kirkwood's contemporaries, his former students, or, like the writer, those who had greatly benefited from correspondence and personal interviews with Kirkwood. Joseph Hirschfelder opened the proceedings with a brief tribute to Kirkwood's influence upon contemporary science and acknowledged the deep sense of personal loss which he and all of the participants felt.

Particularly singular is the fact that the papers presented at this symposium, together with others of a similar nature, were published almost immediately in the November 1960 issue of the *Journal of Chemical Physics*. These papers are prefaced by an excellent

biography of Kirkwood prepared by George Scatchard. Because of this rapid transmission of information from rostrum to print, my remarks here are intended to provide only a skeleton outline and to call attention to the journal articles.

The first speaker, Hirschfelder, described a procedure for generalizing the familiar virial theorems of classical and quantum mechanics. The classical statement of Hirschfelder's "hypervirial theorem" follows directly from the observation that the temporal average of the Poisson bracket for an arbitrary function W of the dynamical variables will vanish. The quantum analogue of this simply involves the commutator of W with the Hamiltonian operator for the system in place of the Poisson bracket. With each choice of W one therefore obtains a condition upon the time—or ensemble—average behavior of the dynamical system. In this way it is possible to generate a set of relationships which must be satisfied by the moments of the classical ensemble distribution function or by the corresponding quantum density matrix. Hirschfelder remarked that this theorem is currently being applied to such diverse problems as transport phenomena, the equation of state of fluids, and molecular quantum mechanics.

Devotees to the rigid sphere should be especially pleased with the prominent role assumed at this meeting by their favorite molecular model. Curtiss and Hollinger, using a method akin to that of Bogolyubov, illustrated that the Enskog modification of the Boltzmann equation for a dense fluid of rigid spheres is consistent with the assumption of molecular chaos. Stuart Rice described an interesting approach to the theory of transport in dense fluids composed of molecules with pair interactions of the Sutherland variety, i.e., a rigid core short-range interaction combined with an attractive long-range portion represented by an inverse power of the separation. Provided that the density and temperature are properly restricted it should be possible to define a coarse graining in time such that in the field of the weak attractive forces a typical molecule will perform a Brownian motion which is only occasionally interrupted by strong core-core collisions. The temporal development of the distribution

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The three-day symposium reviewed in these pages was held last September in memory of the late John G. Kirkwood of Yale University. Prof. Kirkwood, who died on August 9, 1959, was a fellow of the American Physical Society, a member of the Board of Editors of the AIP journal, *The Physics of Fluids*, and an associate editor of the Institute's *Journal of Chemical Physics*. He was Sterling Professor of Chemistry at Yale and was director of the Sterling Chemistry Laboratory.

functions can then be separated into Fokker-Planck contributions associated with the weak interactions and a standard Boltzmann collision integral arising from the impulsive core-core interactions. Rice indicated that the transport coefficients calculated on the basis of this model are intermediate in value between those separately calculated for the weak and strong portions of the pair potential.

B. J. Alder discussed some of the results which he and Wainwright have recently obtained from their high-speed computer program on "molecular dynamics". Their studies of systems containing from four to five hundred rigid spheres have led to two conspicuous conclusions: (1) the existence of the previously reported first-order phase transition and the dependence of this transition upon the number of molecules contained in the representative system are still somewhat uncertain; (2) the "molecular dynamics" description of transport phenomena fully confirms the predictions of the Enskog theory.

A cell model of the liquid state based upon doubly occupied cells of double size was described by Zevi Salsburg. In the (by now familiar) case of rigid spheres this theory was shown to produce pressure isotherms with slight irregularities near the phase transition point predicted by the theory of Kirkwood, Maun, and Alder and observed in the "molecular dynamics" calculations and in the Monte Carlo investigations of Wood and Parker. Salsburg emphasized that his results must be considered somewhat spurious since they depend critically upon the choice of a face-centered cubic lattice in the cell theory calculations.

No summary of the subsymposium on rigid spheres would be complete without some mention of the "scaled-particle" theory of Helfand, Reiss, Frisch, and Lebowitz. Helfand illustrated the formal relationship which exists between the equilibrium properties of a system for which the pair interactions include a rigid core at small separations and a system which is strictly composed of rigid spheres. This relationship was established by a utilization of the distance scaling technique previously applied to rigid spheres by Reiss, Frisch, and Lebowitz. In contrast to Kirkwood's method where an

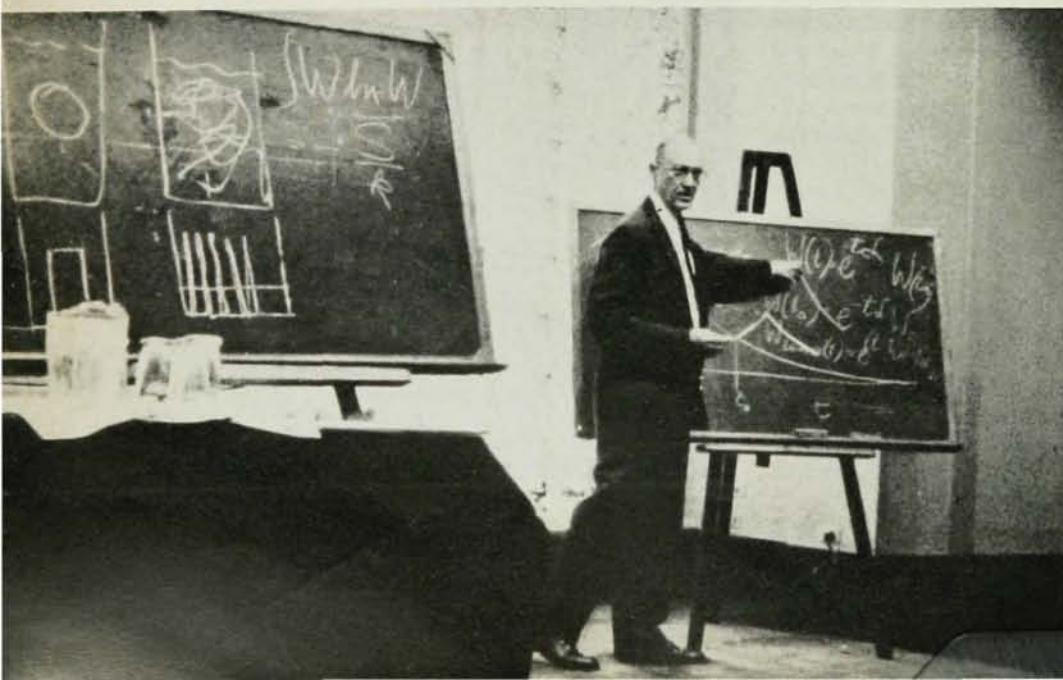




Discussion period at the Kirkwood Memorial Symposium (L. Prigogine standing in center of audience).



Henry Eyring



Joseph E. Mayer

"odd" molecule is coupled into the system by a fraction $\xi u(r)$, $0 \leq \xi \leq 1$, of the actual pair potential, $u(r)$, the scaled-particle theory is based upon the coupling interaction, $u(r/\lambda)$. Helfand showed that by a fairly straightforward extension of the previous rigid-sphere theory it was possible to generate approximations to the thermodynamical properties of the more realistic system with which he was concerned.

An extremely lucid description of the recent progress which has been made in the integral equation method for the calculation of the radial distribution function was provided by Jan de Boer. The approximation procedure he described, that of van Leeuwen, Groeneveld, and de Boer, involves the systematic consideration of progressively more complicated Mayer diagrams. Numerical results obtained from this very elegant theory were shown to be in excellent agreement with experimental data for rare gases. De Boer stated that further calculations are presently being conducted both in Holland and by M. Green at the National Bureau of Standards.

A theory of the diffuse double layer described by Frank Stillinger exhibited several fascinating features. Proceeding from a simple but not unreasonable assumption about the short-range interactions, he managed to perform a calculation of the ionic distributions. At low ionic concentrations Stillinger's results are in agreement with those derived from the usual linear Poisson-Boltzmann equation. However, at high concentrations the distribution of ions normal to the electrode surface is found to alternate in sign, indicative of an incipient lattice formation arising from the repulsive interactions of ionic cores. The zeta potential calculated from this theory becomes negative at sufficiently high concentrations.

The subject of critical opalescence was wrapped into a very neat package by Marshall Fixman, who first demonstrated the equivalence of several earlier theories, and then centered his attention upon the consequences of a modification of the Kirkwood superposition principle which described the correlations of distant molecules in terms of the fluid density at a point midway between their actual locations.

James O'Toole illustrated how Jeans' persistence of velocity calculations for rigid spheres can be extended to more realistic pair interactions, and also demonstrated that the concept of persistence can be applied to the collisional degradation of energy. The friction coefficient obtained from these calculations was related to that defined by Kirkwood.

Entropy production and the approach to thermodynamical equilibrium provided subject matter for several rather spirited exchanges of opinion. The point of view expressed by Joseph Mayer (or at least so I thought) was that the coarse graining in phase space which seems essential to the definition of a nondecreasing entropy function follows as a natural consequence of fluctuations originating at the boundaries of the system. If these fluctuations are small, as they are in

the case of spin echo experiments, one must expect a correspondingly small degree of natural smoothing to occur. This virtual independence of the system from its boundary fluctuations can give rise to an apparent increase in the inferred entropy which may then be followed by its reversal. Prigogine's objection to this seemed to be that the consideration of boundary fluctuations should not in general be a necessary prerequisite to the demonstration of irreversibility. Although I confess my own confusion over the outcome of the lengthy discussion which then took place, Mayer seemed to believe that no difference of opinion actually existed. Harold Grad's comments (beginning with the plea of, "Let me explain what entropy means to me.") tended to confirm my own belief that no complete meeting of minds had been achieved.

Professor Kirkwood's contributions* to modern science have influenced many areas of experimental investigations. This was illustrated by several papers in this symposium which described experimental studies. Dielectric constants of some compressed nonpolar gases were reported in a paper by Cole, Johnston, and Oudemans; values of the Clausius-Mossotti function were compared with theoretical pair fluctuation, polarizability, and multipole moment interaction effects at higher densities. J. R. Cann presented the results of some electrophoretic studies of the isomerization of bovine serum albumin. In a paper by Scatchard, Vonnegut, and Beaumont, new data for the freezing points of aqueous lanthanum chloride solutions were communicated and compared with extended forms of the Debye-Hückel theory. Conductances of tetraalkylammonium tetraphenylborides in acetonitrile-carbon tetrachloride mixtures at 25° C were reported by Berns and Fuoss and the limiting conductances, association constants, and apparent Stokes radii discussed. Flow equations and frames of reference for experimental studies of isothermal diffusion in liquids were discussed in a paper by Kirkwood, Baldwin, Dunlop, Gosting, and Kegeles; tests of the Onsager reciprocal relations and the effect of volume changes on mixing were considered. It was fitting that the symposium closed with a description of a classical treatment of the time dependence of a phase-space distribution function near equilibrium by Donald Fitts, the last student of Professor Kirkwood.

The papers mentioned above represent but a sampling of those presented before the symposium. That others of equal significance and interest have been left unmentioned is an unfortunate consequence of my inability to compress within two pages the contents of some two dozen papers. To prospective readers of the November issue of the *Journal of Chemical Physics* let me, however, heartily recommend "The Surface Specific Heat on an Isotropic Solid at Low Temperatures" by March Dupuis, Robert Mazo, and Lars Onsager; and "On the Theory of the Critical Point of a Simple Fluid" by M. S. Green.

* Thanks are due L. J. Gosting and J. W. Williams for writing this paragraph.