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Remembering Edward Allen Mason (1926–1994)

Edward Allen Mason was born in Atlantic City, New Jersey, on 2 September 1926, the only child of Edward and Olive (Lorah) Mason. The family was hit hard by the depression but recovered well thanks to his father's skill as a salesman for the Real Silk Hosiery Company. His success led to many promotions and transfers to increasingly large and prominent regions of the country. Thus the family moved often, and after some instruction at home from his mother, Ed attended six different schools before he graduated from high school in 1942.

Then after 3 years at Virginia Polytechnical Institute, where he majored in chemistry, he was drafted. Like many college students at that time he took and passed the Navy's Eddy Test that screened candidates for training as radio and radar technicians. After 2 years of learning about and then repairing electronic equipment in the Navy, he returned to VPI, where he graduated in 1947 with a B.S. in chemistry. He did his graduate work in physical chemistry at the Massachusetts Institute of Technology and received his Ph.D. in 1951. His thesis describing an experiment, done in collaboration with John Ross under the direction of Professor Isador Amdur, was titled "The Self-Diffusion of Gases. The System CO_2–CO_2." He stayed at MIT as a Research Associate until he went to the University of Wisconsin in 1952 as a National Research Fellow. During his stay at MIT Ed met and married Ann (Laufman) Mason. They had four children, Catherine, Elizabeth, Sarah, and Stephen, and, at the time of Ed's death, four grandchildren.

Ed's first regular staff appointment was at Pennsylvania State University in 1953 as an Assistant Professor of Chemistry. Next he went to the University of Maryland, where he was an Associate Professor of Molecular Physics from 1955 until 1960, when he was promoted to Professor of Molecular Physics. He became the Director of the Institute in 1966, but he found he did not enjoy the administrative duties that came with the directorship. In 1967 he accepted an appointment as Professor of Engineering and Chemistry at Brown University, where he would be able to devote his

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time to teaching and research. In 1983 he also became the Newport Rogers Professor of Chemistry.

At the beginning of his career when he was a graduate student, Ed set out to discover and learn more about why natural things are the way we find them. He had a remarkable ability to reduce complicated mathematics and massive computer output to their ultimate simplicity through a combination of insight, intuition, and scientific rigor. He could get to the nub of a difficult problem in ways that were particularly appreciated by the physical chemists, engineers, and physicists with whom he worked.

Ed became recognized internationally as an expert in the chemical physics of gases and fluids. He made major contributions to the theory of transport phenomena such as the thermal conductivity of molecular gases in which the internal degrees of freedom and inelastic collisions play an essential role. His pioneering work on the kinetic theory of ion transport in gases inspired a new generation of researchers in many countries, and it carried over to the related field of gaseous electronics. His contributions to transport theory also resulted in a quantitative treatment of gas flow in porous media, now widely used in engineering practice, and a statistical–mechanical theory of transport through membranes that includes, corrects, and extends all previous treatments.

In the last few years Ed's work led to a remarkable advance in how the interactions of molecules can be described not just in dilute gases but in dense fluids as well. A high point for his colleagues was watching Ed's enthusiasm as he showed the almost-perfect agreement with experiments of his and Yuhua Song's theory for a general, simple, analytical equation of state. To find such an equation was the dream of van der Waals, but it was given up long ago as impossible.

In his teaching Ed addressed the whole range of students: freshman, upper-level undergraduates, graduate students, postdoctoral associates, and his colleagues. He often started a class by saying that he did not plan to cover the subject, but to uncover a part of it. He would quote James McNeill Whistler to freshmen, saying, "If silicon had been a gas, I would have been a major general." This was a reference to Whistler having had a brief, unsuccessful stay at West Point at a time when almost all of his classmates had later become generals in the Civil War.

One of Ed's special interests was English and Scottish folk dancing. He was a member of the Pinewoods, Massachusetts, and the Westerly, Rhode Island, Morris Men and danced in the Christmas Revels in Cambridge for many years. He was famous for the back flips he did in the sword dance. Those who had the good fortune to have Ed as a colleague remember him not only for his intellectual powers and the depth and breadth of his knowledge, but also for his warmth and sense of humor. A discussion with

Ed was invariably illuminating and almost always fun. Ed liked to quote Mark Twain: "Always do the right thing. This will gratify some people and astonish the rest." He also liked to remind you of the words by Sgt. Preston of the Yukon, "The scenery only changes for the lead dog." Ed was a regular member of an informal group of Brown chemists who gathered to eat lunch in the office of a colleague. There those present turned to Ed for many things: little-known facts about the Civil War, or as Ed would say the War between the States, and one of his heroes; General Robert E. Lee; comments on outrageous assertions in scientific papers (for instance, troubles people got into by not paying proper respect to the laws of thermodynamics); his almost-endless supply of jokes, some much funnier than others; opinions on possibly trivial but hotly argued points of grammar; and both the historical background and the basic significance of new developments in science.

Giving a short summary of Ed's contributions to science would not be easy. Instead of that, what follows consists of contributions from four people who were his colleagues, students, and friends and knew his work well.

a. Determination of Intermolecular Forces and Their Application to Provide Transport Properties of Air (J. T. Vanderslice, a Long-Time Associate of Ed's at the University of Maryland). Mason's interest in intermolecular forces was first stimulated by his measurements of diffusion coefficients and their interpretation to give potentials for CO_2–CO_2 and CO_2–N_2O interactions. The Amdur group had accumulated a large amount of atomic scattering data on several different interacting systems, but at the time Mason received his Ph.D., the interpretation of the results in terms of intermolecular forces was still unclear. After thinking about it for a few years, Mason finally was able to work out the proper analysis of the measurements so that accurate intermolecular forces could be deduced. A series of papers then followed, first with Amdur and later with Vanderslice as coauthors.

In the post-Sputnik era, a need was seen for the determination of transport properties of partially dissociated gases at high temperatures. Since it was not possible to measure these in the laboratory, it was necessary to calculate them, but this required accurate information on the interaction energies between the atomic and molecular species involved. (Accurate measurements could not be obtained from the standard quantum mechanical calculations, which were costing a fortune!)

Mason and Vanderslice developed an elegant and simple method which allowed them to obtain the necessary interaction energies from spectroscopic measurements on diatomic molecules. They named this procedure "the Rydberg–Klein–Rees method" and used the available electronic spectral data on N_2, O_2, and NO to obtain the interaction energies which were of importance in calculating the transport properties of air in the upper atmosphere. Since the "RKR" method was a WKB approximation, Vanderslice went on to consider higher WKB approximations, and showed that they were negligible. The introduction of this new method stimulated extensive interest in vacuum ultraviolet spectral data, many of which were obtained by Phil Wilkinson and Shelby Tilford at the Naval Research Laboratory in Washington, D.C., in collaboration with Vanderslice. The RKR method is now almost universally used to determine interatomic energies when spectral data are available.

b. Transport Properties and Kinetic Theory (G. T. Evans, Oregon State University, Whose Interest in Statistical Mechanics Was Stimulated by a Course of Mason's at Brown University). Broadly Mason's goal was to provide a kinetic theory of the dilute gas transport coefficients of polyatomic molecules and their mixtures. His concern for a demonstrated utility of kinetic theory and, at the same time, a microscopic physical interpretation were characteristics of his work. At the beginning of his studies, the broad outline of dilute gas kinetic theory existed, but there were few applications to nontrivial molecular systems and little evidence to indicate the accuracy of the Chapman–Enskog theory of transport. Mason's calculations provided detailed and careful comparisons with experimental work that served to test and, in some cases, required him to rethink the basics of transport theory. The impact of his work is broad. For an unbiased perspective, see the Mason citations in the following works: S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases*, 3rd ed., Cambridge, University Press, New York (1970); and J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases*, North-Holland, Amsterdam/New York (1972).

Most of Mason's studies of transport properties have a common thread. They begin with a statement of a macroscopic decay law, e.g., the relationship of the mass flux to a concentration gradient for simple diffusion or the mass flux to the temperature gradient for thermal diffusion. Thermal diffusion was one of his favorite research topics. The proportionality constant in the flux-gradient expressions is a transport coefficient (diffusion and thermal diffusion in the examples cited). Given the phenomenological flux-gradient relation, one calculates the flux starting from a microscopic molecular theory and, in so doing, one derives the transport coefficient.

Typically Mason solved the linearized Boltzmann equation (using Chapman–Enskog methods) to calculate the fluxes as a consequence of the two-body collisions. He published a few papers in which the Enskog corrections to transport coefficients were retained, but density corrections were not his major concern. The bulk of his work on fluids dealt with the binary collision regime, i.e., with dilute gases.

Inside the Boltzmann collision operator is the cross section for the binary collision, and it is here that the molecular characteristics appear. Such characteristics include molecular nonsphericity, vibrational and electronic degrees of freedom, and the intermolecular forces appropriate to dipole, quadrupole, and charged particle systems. Given the cross section, he calculated transport coefficients for thermal diffusion, thermal conductivity, mass diffusion, and the shear viscosity.

On the basis of the transport property calculations of single-component systems, Mason and colleagues extended dilute gas kinetic theory to binary and multicomponent mixtures. Since the intermolecular potential parameters of mixtures were not known, he used various combination rules in order to achieve accurate fittings of transport properties. Mixtures investigated include wet gases and air, as well as others with various polyatomic and monatomic components. The mixture work was performed in collaboration with Joseph Kestin, and through this collaboration, careful and systematic evaluations of the utility of the kinetic theory of gas mixtures became available.

In another area of research, Mason addressed the statistical mechanics of membranes with the specific goal of providing a unified statistical mechanical theory of mass and momentum transport across membranes. The membrane was considered to be one component of a multicomponent fluid and the transport processes were driven by gradients in concentration, voltage, and pressure. Each of these stimulus-induced flows was considered separately in the context of simple systems and the synthesis of these was his theory of membrane transport.

The net effect of Mason's research into the transport properties of gases is by no means to close this field. If, however, one wants to understand the temperature and composition dependence of a dilute fluid (or fluid mixture) of real nonspherical molecules, Mason's work should be consulted.

c. Ions in Gases (L. A. Viehland, St. Louis University, Who Was a Postdoctoral Research Associate Working with Ed at Brown University). Mason's interest in intermolecular potentials and how they govern the transport properties in gases led him into the field of gaseous ion transport. Ions diffuse through gases like neutral particles, but they also respond readily to the influence of an external electrostatic field. The relevant transport coefficient is the mobility, which is simply related to the average ion (drift) velocity through the gas. At low field strengths the diffusion coefficient and mobility are simply related to each other through the Nernst–Townsend–Einstein relation. As the electric field strength increases, however, ion diffusion becomes anisotropic and is characterized by two diffusion coefficients, one parallel (longitudinal) and the other perpendicular (transverse) to the direction of the electric field. Moreover, the magnitudes of the mobility and diffusion coefficients change significantly as the strength of the electric field increases, because different regions of the ion-neutral interaction potential are probed as the average collision energy increases.

Building upon theoretical work of Wannier and Kihara, Mason wrote a notable paper with Schamp in 1958 that allowed for the practical calculation of gaseous ion transport coefficients from realistic models of the interaction potential between atomic ions and atoms. However, their approach was restricted to weak (albeit nonvanishing) electric field strengths. Since this restriction made it impossible to exploit most of the gaseous ion data that were available, Mason left this area of research after producing a few papers in the late 1950s. But in the late 1960s he returned in order to consider special aspects of the problem: ion–ion interactions; deviations from Blanc's law, which governs the transport of ions through mixtures of gases; charge-exchange and quantum-mechanical effects; and models that would allow the atomic ion–atom approach to mimic most of the physics involved for polyatomic systems. These studies complemented the experimental work on gaseous ion transport then being carried out at Georgia Tech, and McDaniel and Mason wrote a book in 1973 that was to serve as the main reference in this research field for the next 15 years.

By the early 1970s, Mason was again ready to attack the main problem in gaseous ion transport theory, i.e., how to handle situations in which the electric field is not weak. Mason and Hahn developed approximate formulas that worked reasonably well for rigid-sphere models of the interaction potential. Whealton and Mason pushed the theory to higher field strengths by expressing the transport coefficients as power series. The breakthrough finally occurred in 1975, when Viehland and Mason realized that all previous work had implicitly or explicitly used the gas temperature to characterize both the ions and the neutral atoms. This is convenient but physically inappropriate, since at high field strengths the small number of ions present have to be characterized, at the very least, by an ion temperature (average kinetic energy) much larger than the gas temperature. Quickly, the standard approaches to describing ion motion through gases became this "two-temperature" kinetic theory and its "three-temperature" extension, where the ions have different average kinetic energies parallel and perpendicular to the electric field.

From 1975 until 1994, Viehland and Mason collaborated in a large number of papers that applied and extended their two-and three-temperature theory. They developed means for testing proposed ion-neutral interaction potentials by comparing computed transport coefficients with experimental results, and they also developed ways to solve the inverse problem and extract, from the experimental data, points on the ion-neutral potential. Perhaps the best summary of the progress made during this time was provided in the 1988 book by Mason and McDaniel.

d. Equation of State for Fluids (R. M. Stratt, a Colleague and Collaborator of Ed's at Brown University). All of the thermodynamic properties of a fluid are encapsulated in the mathematical relationship between the fluid's pressure, volume, and temperature—what is commonly called its "equation of state." It is therefore hardly surprising that an ability to predict such equations of state accurately and with a minimum of empiricism has been so highly prized in engineering applications. More than that, though, an ability to understand equations of state on a purely molecular level, using nothing more than information on intermolecular potentials and the tools of equilibrium statistical mechanics, would mean finally meeting a challenge posed over a century ago by van der Waals—and would signify that one could, finally (!), claim some reasonable measure of understanding of at least the equilibrium properties of liquids and gases.

At the end of his career Mason and a student, Yuhua Song, decided to revisit this problem. Much to their surprise and delight, they were able to make substantial progress in just a few years of work. Making use of modern developments in the perturbation theory of liquid structure and a number of insightful assumptions, they were able to arrive at a remarkably accurate equation of state, one that was suitable not only for noble-gas fluids, but also for both polar and nonpolar molecular fluids. In the process, they and co-workers were able to show that many of the common empirical equations of state that had been used over the years could be thought of as modifications or simplifications of their microscopically derived equations. They were also able to analyze (and in some cases explain) a number of puzzling regularities that seemed to govern the thermodynamics of liquids.

The starting point of their development was the idea, pioneered by van der Waals and put in modern statistical/mechanical form by Weeks, Chandler, and Andersen, that the arrangement of molecules in a liquid is largely a matter of packing hard objects. Attractive forces actually do matter to the thermodynamics, but in the WCA approach, their influence is well described by perturbation theory. Similarly, the fact that true repulsive forces are not infinitely hard can be included in a WCA calculation with the aid of an effective hard-sphere diameter. What Song and

Mason noted though, is that both the attractive forces and the softness of realistic repulsive forces could be treated somewhat nonperturbatively, and in a fashion much simpler and more directly than they had been, by judicious manipulations of the second virial coefficient. The hard-object packing problem that remained was solved by appealing to the known behavior of hard spheres for atomic liquids and, with the help of a suitable generalization, by appealing to the averaged properties of hard convex bodies.

The equations of state that resulted matched rather impressively the available experimental data for fluids ranging from Ar, N_2, and SF_6 to NH_3 and H_2O. Perhaps equally strikingly, they organized the data to the point that Mason and co-workers were able to propose even more accurate equations of state by considering the tiny residual discrepancies. Yet a further bonus was that the predictions (both with and without the additional correction) implied a version of the law of corresponding states capable of collapsing all of the information on the three-dimensional pressure–volume–temperature surface of a fluid into a single master curve for each fluid.

With all of this success, perhaps the most interesting legacy of this work is that it highlighted some questions about liquids that still remain unanswered. The existence and magnitude of many-body forces have now been understood for some time, but when the results from Mason's new equations of state were compared for real and purely pair additive models of liquids, the differences emphasized the fact that the qualitative character of the influence of many-body forces on liquid thermodynamics is still somewhat mysterious. Similar comments are in order about the numerous empirical equations of state that seem to govern liquid behavior. To pick just one example: The form of Mason's equation of state seems to explain the basic reasons why the Murnaghan equation of state works as well as it does, but as Song, Caswell, and Mason pointed out, it fails to explain why the central quantity in the equation, the Moelwyn–Hughes number—should be proportional to the reciprocal temperature. The list of such mysteries that Ed compiled in his last (1993) papers is a fitting reminder of the richness and depth of the equation-of-state problem.

E. F. Greene
Brown University