THE LONG CHAIN FROM KRAMERS'S POLYMER WORK

I thoroughly enjoyed reading the informative article (September 1988, page 26) by Max Dresden on Hendrik A. Kramers's contributions to statistical mechanics. This letter is intended as a "friendly amendment" to call attention to Kramers's seminal article in 1944 on the statistical mechanics of flowing macromolecular solutions.[1] This paper was published in Dutch, because during the German occupation publication in English was not allowed; after the war the *Journal of Chemical Physics* published the complete English translation by Jan J. Hermans and Kramers.

This article showed a grasp of macromolecular kinetic theory that was far more mature and inventive than that of the contemporary polymer scientists. Kramers wrote only one paper in this area, but it is astonishing how much he accomplished. He began by cleverly recognizing that the very difficult *nonequilibrium* problem of getting the phase-space distribution function for a macromolecular solution in a time-independent, potential flow can be made equivalent to a tractable problem in *equilibrium* statistical mechanics. Since he modeled the polymer as a freely jointed bead–rod chain (or "pearl necklace"), he used generalized coordinates and momenta to account for the constraints of constant rod lengths. He then established the kinetic theory expression for the stress tensor as an integral in the chain phase space. Finally he obtained an expression for the zero-shear-rate intrinsic viscosity.

In this development a matrix $g_{\mu\nu}$ plays a crucial role; this matrix is, aside from a constant factor, the reciprocal of the "Rouse matrix," which appeared nearly a decade later and is familiar to all polymer chemists. The Kramers derivation shows quite clearly that the freely jointed bead–rod model for finite chains does *not* obey the random-walk distribution, a point that surprises many polymer chemists even today.

Kramers then went on to show how to extend his theory to freely rotating chains and to branched polymers. He also proved that a flexible ringlike polymer should have a viscosity equal to one-half that of a chainlike polymer with the same contour length. In addition, he considered the flow birefringence of the same system. Finally, he suggested how to extend his work to describe the finite-shear-rate rheological properties; this part of the paper was the starting point for a whole series of papers on polymer kinetic theory by John G. Kirkwood and his collaborators[2] during the late 1940s and early 1950s. These papers, in turn, provided considerable information and inspiration for three books dealing with polymer dynamics and rheology.[3,4] In the third of these books[4] there are many direct references to Kramers (see both the author and subject indexes) that attest to his continuing influence in the statistical mechanics of macromolecules and to the many ways his work could be applied and extended.

Specifically, the Kramers paper provided the impetus for a further development of the phase-space kinetic theory of polymeric fluids (both dilute solutions and melts) under the leadership of Charles F. Curtiss.[5] It also provided the starting point for interesting papers by Eugene Helfand and Nicolaas van Kampen[6] dealing with the freezing-out of vibrational degrees of freedom and the deviations from the random-walk distribution. Marshall Fixman[7] and Ole Hassager[8] also contributed substantially to the understanding of polymer solutions by developing the Kramers theory further. (For additional literature citations see reference 4.)

Because Kramers wrote only one paper on polymer solutions, the enormous contribution of this publication has not received the attention it deserves; specifically, Paul Flory, in his book on the statistical mechanics of chain molecules,[9] made no mention of the Kramers paper.

In a mere 18 pages Kramers set forth key ideas on polymer kinetic theory that have had lasting influence. This paper was well ahead of its

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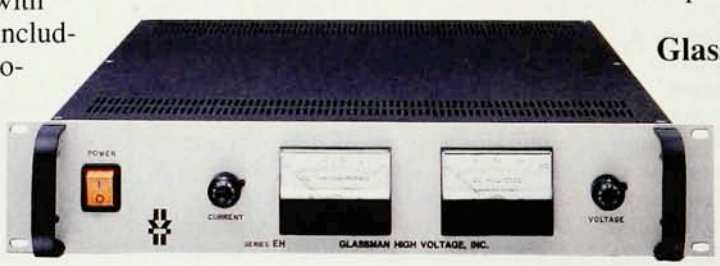

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time, in both physical understanding and mathematical sophistication, and still merits careful study by polymer scientists.

Thanks are due John D. Ferry, Walter H. Stockmayer, Bruno Zimm, Jan Hermans and Nico van Kampen for suggesting improvements to the original manuscript of this letter.

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In a recent article Max Dresden discussed the importance of Hendrik Kramers's contributions to statistical mechanics, even though he wrote only nine articles in this area. In view of this small number of publications, it seems worthwhile to add a few words concerning Kramers's only contribution to polymer statistics. This was a relatively small article, but one that exhibited important characteristics of Kramers's style.

In 1946, Kramers published an article[1] in which he proved that the intrinsic viscosity of a flexible chain molecule follows the Staudinger rule, $[\eta] = KM$. That is, the viscosity is proportional to the molecular weight M of the polymer molecule. This rule played a historic role in the recognition of the existence of large-molecular-weight molecules.

The statistical mechanics of a chain polymer poses the difficulty that one must deal with the connectivity of the segments that are its constituents. Kramers tried an exact treatment of this difficult problem in which he expressed the polymer configuration in a Riemannian space. His was probably the first article in which Riemannian geometry was used in statistical mechanics. A few years later, John G. Kirkwood developed a tensor approach to the same viscosity problem. These appear to be the only two articles in which Riemannian geometry was used for polymer statistics.

I am told that Kramers gave a talk at Cornell University on the subject around 1946. As soon as his talk was over, Peter Debye stood up and remarked that he too had proved the Staudinger rule, in a different but simple way. Indeed, their articles appeared in the same issue of the same journal.

The viscosity rule triggered the development of polymer science, and eventually earned Hermann Staudinger a Nobel Prize. Paul Flory's excluded-volume concept, for which he received a Nobel Prize, also originated from intrinsic viscosity.

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I read with great interest Max Dresden's article on Hendrik Kramers's contribution to statistical mechanics. However, there is one rather serious oversight.

When discussing Kramers's work on the Ising model, Dresden writes: "After World War II . . . he never worked on the Ising model again. . . . He did not . . . contribute to the developments that followed [Lars] Onsager's work." However, in the list of theses completed under Kramers's supervision one finds a 1950 thesis on "Order–Disorder in Hexagonal Lattices" by R. M. F. Houtappel. The main results were published in *Physica*.[1] On reading this paper one comes across yet another example of Kramers's facility in producing elegant mathematical methods: The method used is a simplification of Bruria Kaufman's method, which itself was already an improvement of Onsager's original method. This clearly proves the inaccuracy of Dresden's statement.

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DRESDEN REPLIES: Both Akira Isihara and R. Byron Bird observe that although Hendrik Kramers wrote only one paper on polymer statistics, that paper had an enormous and lasting influence. This observation is in complete harmony with the ideas expressed in my paper: Kramers's contributions to statistical mechanics, few as they are, are gems full of technical mathematical innovations, combined in a most original way with deep physical insight.

I am most thankful to Isihara and Bird for calling attention to yet another one of Kramers's seminal contributions, which like many others has not always received the recognition it deserves. This particular paper was not mentioned in the original article for lack of space, so it is gratifying that these letters give an idea of Kramers's contribution in this area, especially his unusual and perhaps unexpected use of Riemannian geometry.

The thesis by R. M. F. Houtappel to which D. ter Haar calls attention was clearly strongly influenced by Kramers. The elegant mathematics, the ingenious way in which explicit group theory is avoided in a clever adaptation of Bruria Kaufman's method—these are as characteristic of Kramers as his signature. Thus Kramers was certainly aware of and explicitly conversant with the developments in the Ising model that followed the celebrated Kramers–Wannier paper. In that sense my statement that Kramers never worked on the Ising model after World War II is too strong. He clearly stayed informed and thought about it. Still, I believe that the general idea I expressed is probably correct. Comparing Kramers's intense, deep preoccupation with the Ising model during the war years with his subsequent more casual involvement, almost by proxy, indicates to me that his own personal involvement declined sharply if not precipitously. Of course Kramers, even if only casually interested, could make contributions of such depth and brilliance that any totally committed investigator would have been pleased and proud to have made them.

I believe that all the correspondents and I agree that Kramers was an unsurpassed master in using and inventing mathematical procedures that were miraculously suited to the elucidation of physical problems in statistical mechanics.

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8/89

Profiles in Publishing Productivity

We recently completed a study of publishing patterns of PhD physicists trained and employed in the United States.[1] We were particularly interested in the relationship between publishing activity and age. Because the average age of physicists, and scientists in general, has increased dramatically in the past 10–15 years, a concern of US science policy makers is whether this older group is as productive as a younger group was a decade or two earlier. Given the inherent difficulty of measuring research productivity, and given that there is some evidence that publishing is a reasonable measure of productivity,[2] our study focused on the relationship between publishing activity and age. Specifically, we counted the number of journal articles authored in a two-year period. Adjustments were also made to this count for the number of coauthors as well as for the quality of the journal in which each article was published, where quality was measured by the impact the journal has on the science literature as reflected by citation practices.[3] Physicists in the 1973, 1975, 1977 and 1979 Survey of Doctorate Recipients, administered biennially by the National Research Council, were included in the study.[4] Information on their publishing patterns was taken from the Science Citation Index with the cooperation of the Institute for Scientific Information.

Past work by Stephen Cole[5] and by Alan E. Bayer and Jeffrey E. Dutton[6] on age–publishing profiles of physicists suggests that article production increases until early middle age and declines thereafter. Cole's sample was restricted to physicists employed in doctorate-granting departments in the late 1960s, while Bayer and Dutton's sample consisted of physicists employed at colleges and universities during the 1972–73 academic year. A strength of the SDR data base used in our study is that it is drawn from a later period and includes scientists in five employment sectors: graduate academic (universities offering a PhD in physics), nongraduate academic, Federally funded research and development centers, government, and business and industry.

Our results for physicists in academic employment are somewhat different from those of Cole or Bayer and Dutton. In particular, when we grouped our sample by five-year age intervals, we found that for physicists in graduate departments the productivity of the 35–39-year-old group is