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Professor Walter Kauzmann in the late 1960s: how a chance conversation resulted in a thesis chapter, and his simple perspective on polywater

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In the late 1960's I was a graduate student at Princeton with Arthur Tobolsky (Fig. 1). However, my dissertation research topic—polypeptide liquid crystals—was orthogonal to everyone else's in the Tobolsky group at that time, hence, I hung out with the Kauzmann group[1] as they were involved in many aspects of physico-chemical studies of biological macromolecules. While it is difficult to appreciate this today, before the now-ubiquitous LCD was fabricated, very few scientists had ever heard of the juxtaposition of 'liquid' and 'crystal' without an intervening conjunction. None of my fellow graduate students nor faculty I interacted with had any idea what distinguished this curious phase from ordinary liquids. Needless to say, Walter Kauzmann was not among this group.

Fig. 1. The author with Professor A.V. Tobolsky in Frick Laboratory circa 1968.

1. Polypeptides

Professor Kauzmann got used to seeing me around, and on one occasion in 1967 he asked me what I was working on. I told him I was looking at the liquid crystalline phase of concentrated solutions of α-helical, synthetic polypeptides. I brashly went on and told him about a puzzling observation, knowing he would have some unique insights. My predicament involved the sense (right- or left-handed) of the 'cholesteric pitch' exhibited by polypetide liquid crystals: The helical structure assumed by poly-γ-benzyl-L-glutamate (PBLG) is right-handed, independent of the solvent. However,

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[1] I was introduced to the Kauzmann group by my very good friend and contemporary, Kon Ho Cho, alias *Chipamdropus S. Koreus*.

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the sense of the helicoidal supramolecular structure in liquid crystalline PBLG solutions was right-handed in some solvents and left-handed in others. Kauzmann contemplated this for a few seconds and said, 'the grooves made by the benzyl ester side chains on the exterior of PBLG's rigid (right-handed) helical core must change sense when you change solvents. Those grooves would behave like the grooves of real screws: when you interlock the threads of a pair of right-handed screws, the barrier to rotation that you feel when you try to rotate about an axis normal to the interlocked screw axes depends on whether you rotate clock-wise or counterclock-wise. And, it must be this barrier that determines the sense of the cholestreric pitch in the liquid crystalline polypeptide solutions.

About a year after this conversation, Harold Scheraga and coworkers. (Cornell University) published computer simulations of PBLG wherein they noted that there were two low-energy conformations for the side chains [1]. And when I made the corresponding molecular models, it was apparent that one surface exhibited a right-handed groove and the other a left-handed groove. As a result of Kauzmann's brief conversation sensitizing me to the potential role of PBLG's side chain secondary structure, the last chapter of my thesis was titled 'Some Ideas on the Origin of the Helicoidal Supramolecular Structure in Polypeptide Liquid Crystals' [2]. In it I explicitly showed a drawing of a pair of screws with interlocked threads (Fig. 2) along with polaroid pictures of the low-energy side chain conformations of PBLG. Not surprisingly, Kauzmann's simple explanation of the origins of cholesteric pitch in polymer solutions has been 'rediscovered' several times by other researchers over the intervening 35 years.

2. Polywater

It was impossible to resist the excitement sweeping the world of chemical sciences in 1968–1969 concerning a 'new, thermodynamically-stable state of water'—polywater! So I surreptitiously prepared some according to the prescription given by the Soviet scientists Derjaguin and Fedyakin. It could be made simply by letting water condense in quartz micro-capillaries and, as they suggested, the condensate appeared to be very viscous, exhibited a boiling point higher than 100 °C and a freezing point lower than 0°. I gave some to a very precocious undergraduate chemistry major, Gregory Petsko, and he, using the primitive signal-averaging capabilities available to us at the time, eventually succeeded in taking the proton NMR spectrum of those minute quantities of 'polywater' [3]. (In retrospect the spectrum was indicative of what one would expect from an acidic mixture of salts leached from the capillary walls.) But Professor Kauzmann's attitude about this controversial subject was very disconcerting to me and fellow graduate students: throughout all of this scientific furor over a 'new state of water', Professor Kauzmann remained conspicuously calm and detached. His thermodynamically-correct perspective was pragmatic and supremely understated: 'If polywater were real, transatlantic cruise lines would be out of business!'

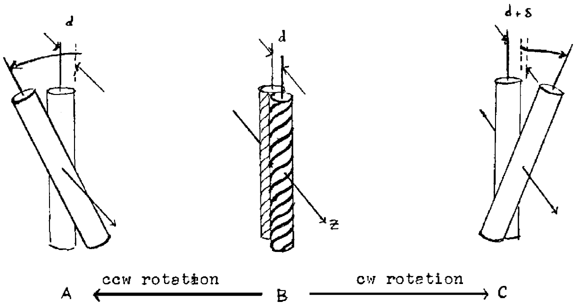

Fig. 2. Illustration of the physical barrier (δ) on rotating clockwise (cw) two right-handed screws with interlocked threads. (Fig. 18 in [2])

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