Forty Years of silica simulations. Where are we now? (With a digression on Al Cooper and the Deborah number)

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In 1964 Aneesur Rahman published his seminal paper on the study of atomic liquids interacting by continuous potentials\(^1\), taking the field to a new world of realistic systems. About a decade later at a Euchem conference on molten salts I listened fascinated as Leslie Woodcock, a recent graduate from Konrad Singer's UK group, described the first molecular dynamics studies on ionic systems - molten sodium chloride. Seeing this as the way to avoid crystallization of simple ionic liquids, I proposed a collaboration. Leslie visited Purdue in 1973 for a discussion and we hatched a plan to use the Purdue University mainframe computers, to test a preposterous idea of applying the new programs (that used Ewald summations for the long range electrostatic forces) to the archetype of glass science, SiO\(_2\). We pretended that it consisted only of ions (Si\(^{4+}\)and O\(^{2-}\)). Phil Cheeseman, then a young programmer in machine language at the Purdue Computer center, expressed interest in the project and soon the project was no longer "tongue-in cheek". As soon as we had chosen the Tosi-Fumi-like interaction parameters that gave the right internuclear separations, everything else fell into place. Leslie had meantime vitrified the KCl of his initial study, and added ionic ZnCl\(_2\). We decided to publish a combined paper. Meantime, Rahman with colleagues Fowler and Narten had looked at an ionic system, the weak field analog of SiO\(_2\) that is beryllium fluoride, BeF\(_2\). With a letter to JCP\(^2\) it became the first known glassformer to be studied by simulation. Our SiO\(_2\) paper\(^3\), which paid attention to problems that the glass field was then worried about, got more attention, and has now been cited >500x. It probably initiated what is now a broad field of geochemical simulations. Many more refined potentials than the simple case explored by us have since been explored\(^4\). The BKS potential\(^5\) which allows partial charges but retains centrosymmetric pairwise additive potentials, seems particularly good, and allows the experimental glass temperature 1473K, to be predicted with good precision from studies made thousands of degrees higher in temperature\(^6\). A new twist was recently added with the evidence\(^6\,\,^7\) that some SiO\(_2\) models provide a companion to water models that show a second critical point, and the possibility of underlying liquid-liquid transitions. This in turn likely relates to the liquid-liquid phase separation so well known in the Li\(_2\)O and Na\(_2\)O + SiO\(_2\) binary systems. Current studies of this problem\(^8\) using BKS and WAC models of silica will be described.


