Forty Years of Silica Simulations. Which Way Now?

C. Austen Angell*

Department of Chemistry & Biochemistry, Arizona State University, Tempe, Arizona 85287

Ten years after Aneesur Rahman’s seminal 1964 paper on simulating liquid argon using computer simulations of atoms interacting with continuous potentials, Woodcock and Singer published the first study of ionic liquids using the same classical mechanical approach. With tongue-in-cheek, Woodcock and Angell with student Cheeseman then studied SiO$_2$ in a simple ionic model using Tosi-Fumi type potentials and were surprised by the degree of similarity to the unusual properties of the “real” silica, liquid, and glassy, they were able to obtain. Since that time, many advances have been made and the field of ionic liquids now embraces geochemical in addition to complex inorganic glass systems. Now it seems that some “silica” models may exhibit water-like second critical points, and then liquid–liquid transitions, and so may serve as new model liquids for liquid polyamorphism studies. Current studies using the realistic van Beest-Kramer-van Santen(BKS) and the simpler Woodcock-Angell-Cheeseman(WAC) potential models will be described. We provide background on silica’s role as a “strong” liquid, and on the criterion for ergodicity breaking which requires the relation $Q_d/T_1$ to hold at the hysteresis peak $T_p$ (coincides with three common definitions of $T_g$).

Background: viscosity and non-Arrhenius kinetics

Silica glass is a remarkable material, for which full appreciation is still arriving. Found in Nature as the famous “Libyan desert glass,” a pale lemon yellow material that is >98% SiO$_2$ (most likely formed by an extraterrestrial object impact$^1$ melting the silica sand desert surface ~26 million years ago). Silica glass is so refractory that until the last millennium it could only be used in combination with other oxides that made it melt lower and flow more easily. But unlike these more easily manipulated derivative glasses, silica glass itself does not crack when heated red hot and thrown into cold water, a consequence of its vanishingly small expansivity.

There have been other, more recent, features that have attracted attention. Silica glass has been seen as the extreme, and most boring, case among glassforming liquids because its viscosity (now that we can measure it), is found to obey the Arrhenius law, in contrast with the behavior of almost all other glassforming liquids. The general (and sometimes extreme) departure from Arrhenius behavior has been one of the most striking features of glassformer behavior. In general, the viscosity seems to be following a divergent path, tending to infinity at a finite temperature $T_0$, according to the well-known Vogel-Fulcher-Tammann (VFT) equation$^2$, Eq. (1) below (which we will use here, notwithstanding the arguments for other (arguably) more successful and less provocative forms$^3$–$^6$),

$$\eta = \eta_0 \exp \left(-\frac{B}{T - T_0}\right)$$  \hspace{1cm} (1)

where $\eta_0$, $B$, and $T_0$ are constants.
The VFT equation is frequently modified to the form

$$\eta = \eta_0 \exp\left(-\frac{DT_0}{|T - T_0|}\right),$$

(2)

because then the parameter $D$ quantifies the departure from the Arrhenius plot when data for glassformers of all known types are condensed into a single plot by $T_g$-scaling of the inverse temperature, as illustrated in Fig. 1. The $T_g$-scaled Arrhenius plot has been widely used to classify glassformer types according to their "fragilities." The most fragile liquids are those with the smallest values of $D$ (Fig. 1a).

Silica has the largest value of $D$ that has been determined, with the exception of glassy water. For SiO$_2$, $T_0$, and O K are about the same so the question of what might happen at low temperatures does not arise. That is, so long as the pressure remains low. When pressure rises to values commonly encountered in the geosciences, however, the situation is quite different. At pressures high enough for the silicon to be forced into 6-coordination with surrounding oxygens, computer simulation studies show the liquid becomes much more diffusive,$^7$ the liquid character changes dramatically, from strong to fragile,$^8$ and accordingly the $T_0$ of Eq. 1, must rise to large values. We tell the story of these early simulations later, but first need to deal with some fundamental issues.

Whether or not the peculiar divergence implied by Eq. (1) for $T$ approaching $T_0$, actually occurs, cannot be determined experimentally because of the intercession of the glass transition, and so, the question becomes the domain of theory. Scenarios ranging all the way from complete return to Arrhenius behavior (the "activated" behavior of Mode Coupling Theory, MCT$^9$) to first order phase changes reaching a low energy, nearly ideal glass state$^{10,11}$ have been proposed. Attempts have been made recently$^{12}$ to bring the relatively new phenomenon of "ultrastable glasses" in under the first order phase change umbrella.

The glass transition is a consequence of what theorists like to call "ergodicity breaking," meaning the way in which the viscous liquids get "stuck" (become configurational arrested) at a temperature where the relaxation time for the increasingly viscous structure exceeds the times we are willing to wait to perform our measurements. With the failure to equilibrate comes a change in temperature dependence of nearly all properties, and a "glass curtain" rings down on the question of the infinite timescale behavior.

### Ergodicity Breaking and the Glass Transition

How are we to understand this ergodicity-breaking behavior? It is universally known that the temperature at which the equilibrium state of the liquid is lost ("ergodicity is broken") depends on the rate $Q$, ($Q = dT/dt$), at which it is cooled. Several prominent glass scientists,$^{13,14}$ including Alfred R. Cooper, for whom this lecture series is named, have noted empiri-

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Fig. 1. (a) Plots of the modified VFT equation (Eq. (2)) for different values of the strength parameter $D$. The plots are extended to temperatures below $T_g$ to indicate the values of $T_g/T$ at divergence hence the ratio $T_g/T_0$ for each value of the parameter $D$. (b) The strong fragile pattern for viscosities of a variety of inorganic liquids.
that, at the temperature where equilibrium is lost, the following relationship appears to hold:

\[ Q \frac{dT}{dt} \approx 1 \tag{3} \]

where \( \tau \) is the structural relaxation time determined from some relaxation process or from the viscosity via the Maxwell relation \( \eta = G_\infty \tau \), where \( G_\infty \) is the shear modulus measured at times “infinitely” shorter than \( \tau \). Cooper and Gupta\(^{13}\) suggested calling this product the Lillie number after pioneering glass physicist, Howard R. Lillie. Here, I would like to argue briefly that this approximate identity is not a mystery but rather is the very essence of ergodicity breaking, subject to testing over many decades of cooling rates.

This is most easily understood by looking first at the simple case of the response of a dipolar liquid, held at constant temperature, to a fluctuating electric field (which is, of course, the standard dielectric relaxation experiment). The response of a dipolar liquid to a fluctuating electric field is complex, which means it has real and imaginary components that correspond, respectively, to storage of electric charge, and dissipation of electrical energy, as explained in any text on liquids. We could equally well consider the real and imaginary parts of the response of any liquid to an oscillating compressive stress.

Let us look at the energy loss component, seen as a function of frequency relative to the real part, (called the dielectric constant, \( \varepsilon' \), in the electric field experiment), in Fig. 2. The “loss” peak, as it is best known, coincides with the decay of the real part to one half of its low frequency value for the simple (single time constant) case illustrated in Fig. 2. Below the loss peak, the frequency of the field is low enough for the molecular reorientation to occur before the field changes sign. Above the loss peak, the field reverses too quickly for this to be true so the molecules never reach equilibrium orientation. At the peak, the frustration is a maximum and the maximum dissipation of energy from the applied field is observed. We have labeled the region below the peak maximum as the ergodic zone, although complete equilibrium is only reached when the field is well below the frequency of the peak.

Maximum dissipation is reached at \( \omega \tau = 1 \), where \( \omega \) is the angular frequency (radians/s) for the simple exponential relaxation being observed in this case. Of course the peak will occur at a different frequency at any other temperature, because the reorientation time is a function of temperature that is fixed by Nature. So where we control the applied field frequency, Nature controls the relaxation time. When the one is exactly the inverse of the other, that is, when we meet the condition

\[ \omega \tau = 1 \tag{4} \]

we cross (continuously) from ergodic to nonergodic behavior (where the ergodicity is determined with respect to the perturbing field that we control).

Turning to the more complex case of breaking ergodicity by temperature change, we recognize that in this case the quantity that we control is the cooling rate \( dT/dt \), designated \( Q^- \). Furthermore, we define the “standard glass” as the glass formed by ergodicity breaking during cooling of the liquid at the standard rate of 20 K/min. The reason for this choice is an empirical one. It is because the enthalpy relaxation time at the standard glass transition, determined by scanning calorimetry using three different constructions (see Fig. 3) is 100 s. The value, 100 s, is also the relaxation time chosen by relaxation spectroscopists to define the glass transition temperature.

As we control the cooling rate \( Q^- \), we must look for a quantity with the same dimensions, controlled by Nature if we wish to find an equivalent to the ergodicity-breaking criterion noted in Fig. 2. The quantity that, on entering into an equation like Eq. 4, yields the value unity is, of course the quantity already there in
Eq. (3) (the empirical relation). It is indeed a quantity fixed by Nature, just as much as is $\tau$ in Eq. 4.

All that is missing now is the peak about which the transition from “tending ergodic” to “tending nonergodic” occurs in the cooling experiment. The peak is not hard to find. It is what has been called the “hysteresis peak” of the glass transition, see for example, Ref. 17 — namely the difference between the liquid heating and cooling curves for some extensive property, when measured during cooling and heating at the same rate. Known for the case of volume since the beginning of glass science, these have been studied most systematically for the enthalpies of glassformers of different fragilities. $^{18}$ Figure 4, taken from Ref. 18 shows the enthalpy hysteresis peaks for a series of molecular liquids ranging in fragility $m$ from 146 to 35.5 where

\[ m = \left( \frac{E_a}{2.303 \times RT_g} \right) \]

Here, $E_a$ is the apparent Arrhenius activation energy, taken at $T_g$.

The peaks are not symmetric but smear out on the nonergodic side, just as the dielectric loss curves spread out in the case of nonsimple glassformers with nonexponential and nonlinear relaxation functions. $^{19}$ For a single relaxation time process, the peak must be more symmetrical.

Elsewhere, we will show how the relation $Qd\tau/\,dT \approx 1$ holds at the hysteresis peak for experiments conducted over 11 orders of magnitude in $Q$.

It can be seen from this relation that when the liquid behaves according to the Arrhenius relation rather than according to an equation like Eq. (2) with
small $D$ value, the Q-dependence of the glass transition (represented by the hysteresis peak), will be large relative to that of fragile liquids. However, for strong (network) liquids like silica, a new problem arises. The hysteresis peaks determined by calorimetry, (even using calorimeters suitable for such high temperatures), would not be determinable for a quite different reason. When the silica is really dry, (as in a computer simulations with no water in the computed sample), there is very little detectable change in heat capacity at the experimental $T_g$ of 1500 K (see next section).

Of course, to check the correctness of the argument, based on Eq. (4), that strong liquids must have large changes of $T_g$ with cooling rate, it is not necessary to make enthalpy measurements. Any other measurement of the glass temperature would be sufficient for that purpose. The compressibility of liquid silica near ambient pressure is large, so the study of density fluctuations frozen in at $T_g$ during cooling at different rates would be suitable for study. The sensitivity of $T_g$ to the cooling rate at which it occurs is a well-known feature of silica glass and others, like albite, that lie at the strong liquid end of the fragility spectrum.

Liquid and Glassy SiO$_2$ by Computer Simulation

Silica, the archetypal glassformer, was the first glassformer to be studied in detail by molecular dynamics computer simulation methods (although the network of its analog compound BeF$_2$ had been earlier the subject of a paper by Rahman et al.\textsuperscript{21}). Actually, this approach to understanding liquids, (essentially using the calculated forces acting on each constituent particles of the liquid, and Newton’s equations, to integrate the motions of all the particles), should be called “ion dynamics” computer simulation for the cases of interest to us in this study. The first simulations of silica reported by Woodcock et al.\textsuperscript{7} literally treated the constituent particles as bare ions of charge +4 for the silicon and −2 for the oxygen.

In 1973, Woodcock\textsuperscript{22} presented his first MD simulations of liquid alkali halides to an astonished Molten Salts meeting in Europe. The realization that, in these calculations, the cooling rates could be made arbitrarily large, inspired the present author to invite a collaboration to study the glassy states of the liquid alkali halides, which would represent the simplest possible ionic glasses. Purdue University at that time had an advanced computer center (CDC-6500 !), and a young assembly language programmer, Phil Cheeseman, expressed interest in joining the challenge. Using his assembly language skills, Cheeseman optimized the Woodcock program for alkali halides which employed, for the force calculations, the potentials advanced by Fumi and Tosi.\textsuperscript{23} The outrageous idea arose of simulating the classical glassformer SiO$_2$ using the same form of interionic interaction for the silicons and oxygens. Although the idea of treating this classical covalent network material as a collection of bare ions seemed sure to attract ridicule, we proceeded with the computation, arbitrarily adjusting the parameters of the potential to match, as well as possible, the radial distribution functions for laboratory silica. When the properties of the liquid state were calculated, the laughing stopped because they were reasonable. The diffusivity showed the water-like anomaly (ion diffusivities increasing with pressure) that had recently been found experimentally for GeO$_2$ by Kushiro,\textsuperscript{24} and the diffusivities themselves were in reasonable agreement with values extrapolated from lower temperatures using the Eyring equation to convert viscosities to diffusivities.\textsuperscript{25} Furthermore, the compressibility of the liquid agreed with that assessed by Renninger and Uhlmann\textsuperscript{26} from the X-ray scattering from density fluctuation frozen into the glassy state of silica. We decided to publish and to our surprise, we had no difficulty getting the paper accepted. It was treated with interest and generosity, and despite an error in reporting the parameters of the potential, has now been cited over 500 times. I still remember the awe with which we watched the collective “breathing” modes of the network using 3D projections, and following the individual ions (each with an identity number, as they negotiated their diffusive movements by successive hops between coordination shells — as witnessed in 2D in Fig. 5).

Many papers by others followed, using different and more sophisticated potentials, culminating in the remarkably successful van Beest-Kramer-van Santen (BKS) potential\textsuperscript{27} which manages to faithfully reproduce the behavior of laboratory silica by trading in some of the ionicity of the our (WAC) potential for a compensating van der Waals-like short range attraction in the Si-O potential. It retained the idea of the essential ionic character of the individual particles. We will refer later to some other interesting features of the simulations executed with this potential, particularly a high temperature peak in the heat capacity, that lie beyond
the reach of experiment. These same features are also found in an interesting exaggerated form in simulations with the original WAC potential, and this is reviving an active interest in the WAC form of potential, not for the purpose of realistically simulating the laboratory substance, but for the distinct purpose of charting the way to an ionic model that manifests the exotic property of second criticality and equilibrium polyamorphism (see below).

Rather than refine the WAC potential, we preferred to follow the WAC silica paper with a study of the more geochemical aluminosilicate system, albite. I remember seeing the need for this in a flash of urgency while on the way to Paris, and then phoning Phil (Cheeseman) late at night Indiana time, to urge him to drop everything he was doing on sodium silicate glasses (which Tom Soules — also at Purdue — but working in a different group, had already been programming) and instead substitute half of the silicons with the charge equivalent combination Al$^{3+}$ + Na$^+$, in order that we could start the field of geochemical simulations. Phil saw the point immediately. By the time, I was back from Paris, Phil, (aided by a very bright new aeronautical engineering undergraduate assistant, Sina Tamaddon), could show me the most interesting feature of this new system. This was the way the alkali cation, Na$^+$, responded to increasing pressure in exactly the opposite manner to that of the network cations, Al$^{3+}$ and Si$^{4+}$ which, like, Si and O in silica itself, became more mobile as the density increased. It won immediate publication in Science.$^{28}$ The behavior of Na$^+$ was perhaps the most spectacular failure of the Stokes–Einstein equation witnessed to date. It is not without interest, here, that when I next caught up with Sina about 20 years later, he had become part of Steve Jobs’ inner circle, first at the NEXT computer company and then back at APPLE when Jobs returned to turn the troubled company he had founded, back to profitability (which he did by importing the innovations from NEXT into the prodigiously successful IMAC desktop - all part of Apple’s history now).

The next step in the exploitation of the simple form of the WAC potential came as a consequence, and follow-up, of the second critical point hypothesis for understanding the provocative anomalies of supercooled water — one of the world’s really bad glassformers. Supercooled water had captured many people’s interest because of Robin Speedy’s demonstration that the compressibility (which he had succeeded in measuring down to 26$^\circ$C below freezing point$^{29}$) was showing all the trappings of the so-called critical divergences associated with critical points. Furthermore, Speedy showed that many other properties of water were following the same power law equations, all with the same divergence temperature,$^{29}$ 228 K (or $-45^\circ$C). What could this mean?

Robin wrote a fascinating paper$^{30}$ linking it to the existence of a spinodal limit to the stability of water that begins as a negative pressure instability of the liquid to stretching. All liquids behave this way at temperatures below the familiar liquid-gas critical point, and this aspect is predicted by such simple equations of state as the Van der Waals equation. But in the case of water at temperatures close to the intersection of the extrapolated density maximum and the Van der Waals-predicted liquid-gas spinodal, this latter spinodal reverses course and comes back to positive pressures. Robin had a coherent interpretation of what had originally been a purely empirical prediction of the best available engineering equation of state for water.

In 1991, Peter Poole in the group of Gene Stanley was trying to verify Speedy’s hypothesis using a molecular dynamics program for water based on the pairwise additive water–water interaction potential known as ST2, but was instead finding that the temperature of maximum density turned around before reaching the liquid-gas spinodal, thus apparently invalidating the
Speedy hypothesis at least for the ST2 potential. For this potential, something more interesting was pos-
tulated, in a famous paper by Poole, Essman, Sciortino,
and Stanley. The new postulate was that water was
characterized by the existence of a second critical point
lying at positive pressures and creating a ripple effect
through supercritical fluctuations that gave rise to all
the anomalies that had been exciting people’s curiosity.
Stanley’s reputation as the guru of critical phenomena
helped give the hypothesis credibility and a rash of
papers both pro and con rapidly followed — but our
concern must be with the influence of this hypothesis
on the simulations of silica.

I had the good fortune that Peter Poole, of the
previous paragraph, chose to follow his Ph. D work on
the critical point hypothesis with a postdoctoral fellow-
ship in our laboratory. In view of the similarity of
anomalies, for example, density maxima in silica and
water, it was natural to raise the question of whether or
not silica might also be subject to critical fluctuations.
The smoking gun for criticality in the case of water
had been the flattening out of the pressure versus vol-
ume relation as described by the van der Waals equa-
tion for the critical temperature. Peter organized us to
purchase the new breed of IBM RISC computers and
proceeded, with contributions from student Mahin
Hemmati, to follow the isotherms for WAC silica to
lower and lower temperatures. Although we failed to
reach low enough temperatures to identify the existence
of a critical point, the isotherms were flattening out
sufficiently to warrant a Physical Review Letter on the
subject and to encourage Peter, in his next position in
charge of a major computational facility in Canada, to
push the subject further. In collaboration with visiting
professor Francesco Sciortino from the University of
Rome, and student Ivan Saika-Voivod, Peter published
two new papers, in 2001 and 2004, postulating
the occurrence of second critical points in each of the
WAC and BKS models, although in each case
the deduced critical points still lay out of reach below
the accessible range of the simulation.

Strong Liquids and Lambda Transitions

Apart from a demonstration that the BKS potential
had the ability to predict the phase diagram of silica
with stishovite, coesite, and quartz polymorphs in the
correct relationship, the subject of critical points in
silica rested until a new motivation came into play in
2010. We had been lured into the subject of disorder-
ing phenomena in binary alloys (specifically Co-Fe
1:1), because of a phenomenon that is apparently a
glass-like transition that had long ago been observed as
the slow-cooled alloy was being heated more rapidly
toward its order–disorder transition (see Fig. 6). Because our study of this alloy showed relaxation kinet-
ics typical of an ideal strong glassformer, we had
become possessed with the idea that strong liquids were
not just the extreme of the fragile-strong spectrum of
glassformer behaviors but were actually the opposite
of the fragile liquids. By opposite, we mean that in these
strong liquid cases, the glass transition is being
approached from above despite a decreasing structural
correlation length whereas, with fragile liquids, the
opposite was the case (as many theorists had been sur-
mising). We saw fragile liquid behavior as an analog of
the behavior of the alloy (order–disorder) systems as
temperature decreases from above the lambda tempera-
ture (Fig. 6), where the increasing correlation length is
well established in the standard Ising model.

Fig. 6. The lambda transition in Co-Fe observed calorimetrically
during temperature upscan after slow cooling, showing
structural heat capacity recovery during heating. The glass-like
transition was shown to obey Arrhenius relaxation kinetics,
typical of a very strong liquids, or plastic crystals, see below.
A further and useful analogy was recognized here. We noticed that (1) in the alternative center-of-mass-ordered systems known as “orientationally disordered crystals” (ODC’s) or “plastic crystals,” there is also found an analog of the strong-fragile pattern that characterizes the glassformers (see Fig. 7), but that the majority of systems are concentrated toward the “strong” limit of the pattern, and (2) in the cases of the “strong” plastic crystals with no melting points (e.g., C_{60}) or with melting points far above their feeble glass temperatures, the systems encountered the same sort of lambda transitions that the alloy systems exhibited. Accordingly, we wondered if perhaps this was somehow the explanation of the strong behavior of silica and other members of the glassformer family that obeyed, or nearly obeyed the Arrhenius equation (with a common high temperature limit of $10^{4.5}$ poise). Armed with the additional recognition that systems with critical points, including the classical gas-liquid cases, share the same characteristic lambda form of heat capacity, we came back to the question of whether the strong liquid silica would indeed “turn lambda” if studied at the correct pressure and with sufficiently long simulation times. We already knew that WAC silica had a heat capacity maximum at temperatures where the diffusivity had water-like values, and a weaker version of the same heat capacity behavior was seen in the BKS system studied by Scheidler et al.,\textsuperscript{38} when all the data points to which they had access, were plotted.\textsuperscript{39} This was observed at ambient pressure, and the question of what could happen at higher pressures became a burning one.

With access to a new fast graphic card-enhanced cluster at ASU, we began a new effort on the WAC model pressure versus volume relation and came close enough to seeing a van der Waals loop for us to claim its existence and then use the observation to theorize further on the existence of liquid–liquid transitions (viz., polyamorphism) at subcritical temperatures.\textsuperscript{39}

This speculation was taking us far out on a limb, and Erik Lascaris, student of Gene Stanley (who was now embroiled in a new controversy on the water criticality question due to skeptical, questioning papers from Limmer and Chandler\textsuperscript{40,41} who attributed the anomalies of water to imminent crystallization) decided to enter the effort to clarify the behavior of the silica models. Erik and the Stanley group had command of superior computational capabilities by their access to the Boston University supercomputer — which brings us to the current interesting stage of development of the simulations with the WAC type of potential and their distinctions from the BKS model.

**WAC-Like Models of Silica as Model Ionic Liquids with Effective Critical Points and Liquid–Liquid Transitions**

In this current stage, the WAC model finally sheds the remaining vestiges of a model of laboratory silica and morphs into an approach to realizing the elusive existence of true criticality (and then polyamorphism) in an ionic model liquid.

As background to this section we note that, although there has been controversy concerning the existence of second critical points underlying anomalies in supercooled water and other liquids, there is general accord that there are liquid models in which there is indeed a second critical point between high and low

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**Fig. 7.** Strong-fragile pattern behavior of relaxation times in plastic crystals showing concentration of examples at the “strong” end of the spectrum of behaviors. (from Bauer et al.\textsuperscript{37}).
density liquid or fluid phases. Models of the genre of Hemmer-Stell, with shoulder potentials, and Jagla, with ramp potentials, exhibit distinct liquid phases that are favored by high or low densities, respectively. In a renewed exploration of these, a valuable tool for identifying the presence of a second critical point in the liquid domain was developed. This is what might be called the “isochore crossing” diagnostic. If a critical flattening of the pressure versus volume (or pressure versus density) occurs, then the simpler-to-simulate pressure versus temperature isochores will show a meeting point near, but above, the critical temperature. When unstable states are tolerated because the system is too small to accept two-phase coexistence, then the isochores will cross. We will show an example below, but first need to emphasize that when an attractive well is added to the Jagla potential, a critical point which otherwise resides at 0 K, moves to positive pressures, and as first shown by Gibson and Wilding. It can even be found above the melting point for a range of values of the ratio of the two length scales characterizing the potential. This “attractive Jagla” model has been explored in great detail by Stanley, Buldyrev, and their coworkers who were able to see the heat capacity spike associated with supercritical enthalpy fluctuations, clearly separated from the kinetic glass transition — a feature not seen in simulations previously. The attractive Jagla model is only water-like insofar as it can exhibit both a density maximum and anomalous fluctuations. By contrast, the slope of the liquid–liquid coexistence line is the opposite of that for water, meaning that pressure increases will decrease the diffusivity rather than increase it as in the case of water.

The new work in collaboration with the Stanley–Buldyrev group turned immediately to the isochore crossing diagnostic in search of clarification of the issue of proximity to a critical point. The verdict is clear. The WAC model is indeed close to criticality (but in need of a small bias to be unambiguous) while, for the BKS model, a critical point is nowhere in sight. Other criteria, such as the lack of coincidence of maxima in response functions, supported the absence of true criticality in the WAC system.

The contrast in behavior between the case of WAC silica and the clear-cut case of ST2 water is seen in Fig. 8. In the case of ST2 water, a second critical zone was confirmed by multiple free energy calculations presented in a recent Nature paper. (a) Fig. 8. Isochores for the WAC model of silica compared with those for the ST2 model of water. The isochores converging in the case of water is consistent with the demonstrated location of a critical point and lower T L–L coexistence zone. However, in the case of WAC silica, the isochores only approach and do not cross. (reproduced from refs by permission).
The question arises as to which changes in interaction potential might tip the WAC system into criticality. This question was considered in Ref. 49 where the suggestion was made to impose a small tetrahedral bias on the system by penalizing any nonlinear Si-O-Si angles (by analogy with the Stillinger-Weber potential for liquid silicon\textsuperscript{52}). However, there turns out to be an even more direct method that will be described in a forthcoming paper (E. Lascaris, unpublished work) in which not only will access to a critical ionic system be gained, but also control of the critical pressure will be demonstrated, and a surprising analogy to the still-unresolved case of real water\textsuperscript{53,54} will be recognized.

Concluding Remarks

The study of the classical glassformer, SiO\textsubscript{2}, both by laboratory and computer simulation methods, has proven a fascinating and rewarding activity in the author’s experience, with insights being gained into many important aspects of liquid state physics and glass science. There remains the relation to the new phenomenon of ultrastable glasses\textsuperscript{55,56} to be brought into the conceptual landscape which, notwithstanding a recent attempt,\textsuperscript{12} remains a major challenge for the future. In view of the absence of evidence for a critical point in the BKS model,\textsuperscript{49} which reliably predicts the glass temperature for laboratory SiO\textsubscript{2},\textsuperscript{38,53} it will be interesting to see whether it might be possible to obtain an ultrastable form of SiO\textsubscript{2} by the controlled substrate temperature vapor deposition technique. In view of the predominance of fragile glassformers among the ultrastable glass cases, and of the recent observations on the moderately strong glassformer, glycerol,\textsuperscript{57} we would expect not, but it is a question that can only be answered by experiment.

On the other hand, it has been argued that even a weak tendency to critical behavior in a single component can be amplified in appropriate binary solutions into a physical phase separation under deep subliquidus conditions.\textsuperscript{38,59} An example in practice is the generation of a separate, pure LDL water phase during cooling of a pressurized dilute solution of LiCl in water.\textsuperscript{60} Long ago, the author and colleagues\textsuperscript{61} raised the possibility that this might provide a rationalization for the precipitation of pure SiO\textsubscript{2} from the sodium and lithium oxide + silica solutions,\textsuperscript{62} when there is little evidence for the positive heats of mixing that normally provide the rationale for liquid–liquid phase separations. Prudently, this heterodoxy was only published in the proceedings of a Bulgarian Glass Society Conference, but perhaps its time will soon be at hand.

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Note added in proof

We wish to make four additions to the works cited in this article, while emphasizing again that this is largely a personal account and makes no pretense to being a full review of what is now a rather large field. We should have mentioned the first proper review of the application of computer simulation methods to the field of glass science, which was that of Angell, Clarke and Woodcock in 1981,\textsuperscript{63} and also the comprehensive chapter on glass structure and its modeling by computation in the 4th volume of the treatise, Glass Science and Technology, by Tom Soules in 1991. This work included original studies on cooling rate effects on vitrification of SiO\textsubscript{2}.\textsuperscript{64} Soules’ first paper from 1979 is also cited. Finally, some novel aspects of silica and its binary solutions were contributed by John Kieffer, who used the absence of boundaries in periodic box simulations to study glassy WAC SiO\textsubscript{2} under negative pressure up to the mechanical stability limit of -7GPa at which it suddenly cavitated to yield a fractal distribution of hole volumes.\textsuperscript{65}

References


