Tunable Liquid-Liquid Critical Point in an Ionic Model of Silica

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Recently, it was shown that the Woodcock-Angell-Cheeseman model for liquid silica [L. V. Woodcock, C. A. Angell, and P. Cheeseman, J. Chem. Phys. 65, 1565 (1976)] is remarkably close to having a liquid-liquid critical point (LLCP). We demonstrate that increasing the ion charge separates the global maxima of the response functions, while reducing the charge smoothly merges them into a LLCP, a phenomenon that might be experimentally observable with charged colloids. An analysis of the Si and O coordination numbers suggests that a sufficiently low Si/O coordination number ratio is needed to attain a LLCP.

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Tetrahedral liquids tend to display a range of phenomena that are anomalous in comparison to "simple" liquids [1]. The showcase example here is liquid water, which displays a large number of anomalies, such as an increase of the self-diffusion upon compression (diffusion anomaly) and an increase of the density as it is cooled (density anomaly). In water, many of these anomalies are highly pronounced in the supercooled regime, far below the melting line. Of particular interest are the seemingly divergent behaviors of both the isobaric heat capacity C_P [2,3] and isothermal compressibility K_T [4] upon cooling. Unfortunately, these experiments are limited by homogeneous nucleation, and crystallization rapidly occurs as the temperature approaches −40 °C [2–4].

To explain both the anomalies and this divergent behavior, several scenarios have been proposed [5–7], among which the liquid-liquid critical point (LLCP) scenario [6] has received the most attention [8,9]. According to this scenario, two metastable liquids exist deep in the supercooled regime: a high-density liquid phase (HDL) that is highly diffusive and a low-density liquid phase (LDL) that is more structured and less diffusive. These two metastable phases are separated by a first-order-like liquid-liquid phase transition (LLPT) line that ends at a critical point. In the one-phase region beyond any critical point, the response functions remain finite and display a locus of maxima or minima that near the critical point merges with the locus of correlation length maxima, known as the Widom line [10–12]. According to this scenario, it is the response function extrema originating from the LLCP that account for many of the anomalies of water.

The LLCP scenario could also explain the anomalies found in other tetrahedral liquids. For example, a LLCP has been found in the Stillinger-Weber model for liquid silicon [13,14]. Another candidate is liquid silica, SiO_2. Simulations of the van Beest–Kramer–van Santen silica model [15] and the Woodcock-Angell-Cheeseman (WAC) silica model [16] show hints of a possible LLCP at low temperatures [17–19]; however, more recent studies have questioned its existence in these models [20,21]. Nonetheless, in the PT plane the isochores of the WAC model are remarkably close to crossing. As the crossing of isochores is a clear indicator of a phase transition [20,22], one may therefore conclude that the WAC model is remarkably close to having a LLCP.

It is important to note that the presence of anomalies does not necessarily imply the presence of a singularity [7], and it is currently unclear under what exact circumstances a liquid would be able to have a liquid-liquid transition. This, together with the fact that LLCPs are notoriously hard to measure in experiment, has led to an intense debate about the existence of such a critical point in water [23–27], and even the general existence of liquid-liquid phase transitions in one-component liquids continues to be questioned [23]. It is therefore important to investigate the conditions under which a LLCP could arise.

Because the WAC silica model is close to criticality, it may help us understand LLCPs in tetrahedral liquids. In this Letter, we modify the WAC model to include a tunable LLCP. Silica, as modeled by the WAC model, consists of a 1∶2 mixture of Si^{+4} and O^{-2} ions without any explicit bonds. Apart from the electrostatic force, the ions also interact with each other via an exponential term:

$$U_{\mathrm{WAC}}(r_{ij}) = \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}} + A_{ij}\exp(-B_{ij} r_{ij}). \qquad (1)$$

Here the subscripts $i, j \in \mathrm{Si, O}$ indicate the species of the two ions involved, and q_i is the charge of each ion ($q_{\mathrm{Si}} = +4e$, $q_{\mathrm{O}} = -2e$). Simulations are performed with $N = 1500$ ions and run for at least 10τ, with τ the approximate equilibration time defined as the average time it takes for an O ion to move twice its diameter of 0.28 nm. At the lowest temperatures, the simulations run up to 50 ns. Further details of the implementation, as well as the values of parameters A_{ij} and B_{ij} (which are all positive), can be found in Ref. [20].

We modify the WAC model by adjusting the charges by a few percent and keeping all other parameters unchanged. In Fig. 1, we consider the behavior of the isochores and the

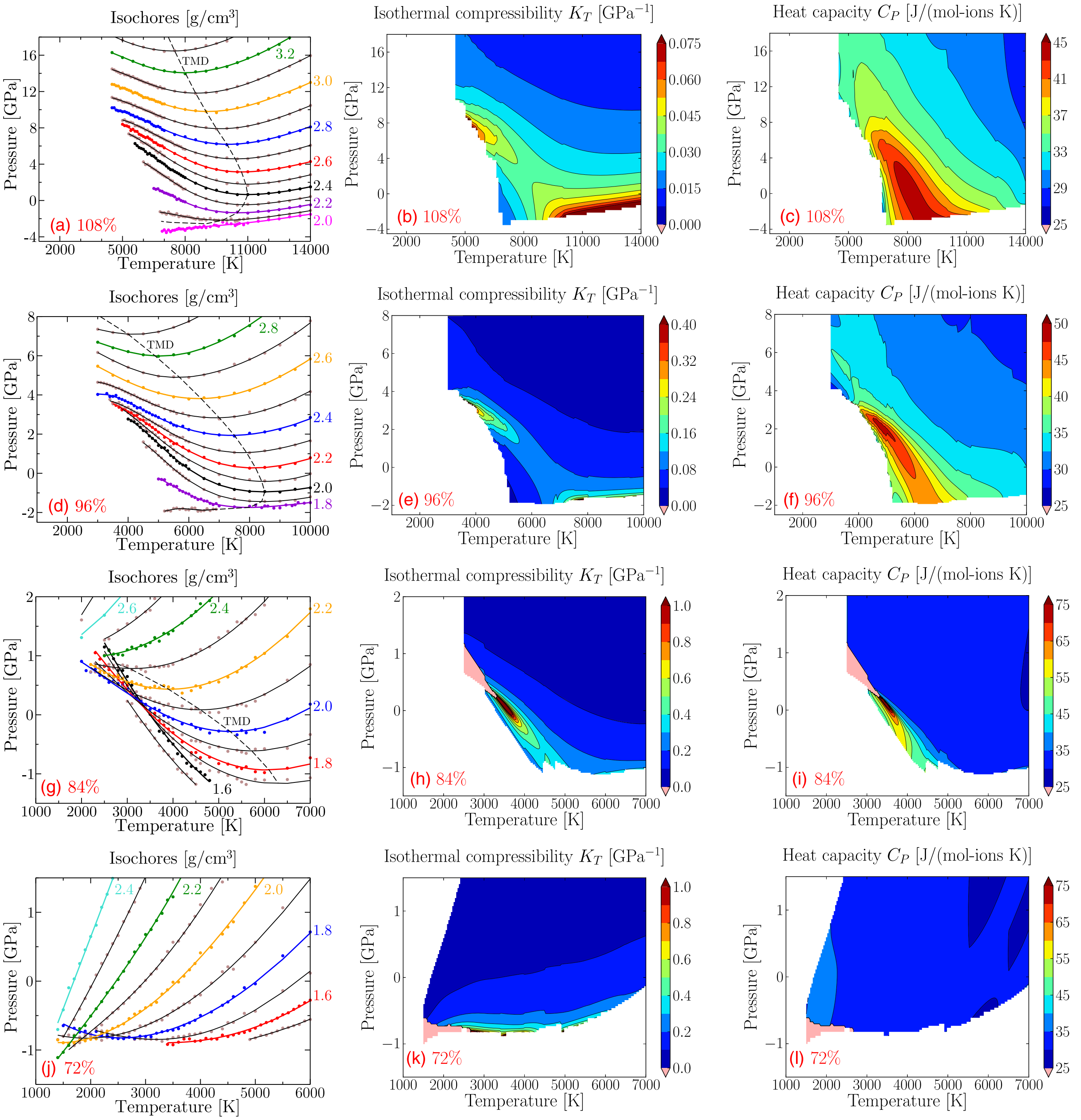

FIG. 1. Adjusting the charge of the ions in WAC allows one to create or destroy a LLCP. Clear signs of a LLCP are (i) the crossing of isochores and (ii) when there is a sharp increase of the response functions. In the thermodynamic limit, if a LLCP is present, then the isochores cross at the same state point as where the response functions diverge. For a finite system, all response functions merely show a large maximum near the LLCP. Left column: Isochores, with matching colors indicating approximately equivalent isochores (red being the isochore that goes through the K_T maximum). Dashed lines indicate the TMD, below which there is a density anomaly: The density *increases* upon heating. Center and right column: Isothermal compressibility K_T and isobaric heat capacity C_P, with the pink area indicating the liquid-liquid coexistence region. Top row: When we increase the ion charge, the isochores approach each other but do not cross, and both K_T and C_P display a large maximum but at different state points. Second row: Upon increasing the charges, the isochores come closer, while the K_T and C_P maxima start to approach each other and grow in magnitude. Third row: Below $f_q \approx 0.94$, the isochores cross and the response functions have maxima at the same state point: the LLCP. Bottom row: Reducing the charge even further moves the LLCP to below the liquid-vapor spinodal.

response functions of the modified WAC model with 72% of the original charge ($f_q = 0.72$, i.e., $q_{\mathrm{Si}} = +2.88e$ and $q_{\mathrm{O}} = -1.44e$), as well as 84%, 96%, and 108%. All plots are limited at low pressures by the liquid-vapor spinodal and at low temperatures by the glass transition line (here taken to be the point where the oxygen diffusivity drops below $D_{\mathrm{O}} < 10^{-7}$ cm^2/s).

The model has both a density anomaly and a diffusion anomaly for all values of f_q considered here. The density increases upon heating at temperatures below the temperature of maximum density (TMD), indicated by the dashed lines in Fig. 1. The edge of the diffusion anomaly lies outside the regions shown in Fig. 1 and is therefore not marked (i.e., for all state points visible in Fig. 1, the diffusivity increases upon compression). Both anomalies disappear at high temperatures and high pressures.

In the top row [Figs. 1(a)–1(c)], we consider what happens to WAC when we *increase* the charges to 108% of their original value ($f_q = 1.08$). The isochores approach each other upon cooling [Fig. 1(a)], which is mirrored by the presence of a large K_T maximum at the same location in the PT diagram [Fig. 1(b)]. Although this would imply the possible existence of a LLCP at low T around $P = 8$ GPa, consideration of the heat capacity C_P throws this in doubt, because it attains a global maximum at a significantly different location: near $(T, P) = (8000$ K, 0.7 GPa$)$ [Fig. 1(c)]. If a LLCP were in fact present, all response functions would diverge upon approaching it.

From Figs. 1(b) and 1(c), it is not immediately clear that the C_P maximum and K_T maximum are connected. However, by reducing the charge to 96% ($f_q = 0.96$), we see in Fig. 1(d) that the isochores move closer to one another, that the K_T maximum grows in magnitude [Fig. 1(e)], and that the global C_P maximum moves towards the K_T maximum [Fig. 1(f)]. Ultimately, once the charge is reduced to below approximately 94%, a clear LLCP appears. A particularly clear example is $f_q = 0.84$, shown in Figs. 1(g)–1(i), where the isochores cross at the critical point and the C_P maximum merges with the K_T maximum at the same state point. Reducing the charge further lowers both the critical temperature T_c and the critical pressure P_c until the LLCP disappears below the liquid-vapor spinodal [Figs. 1(j)–1(l)].

The results shown in Fig. 1 raise the obvious question: Why does reducing the charge introduce a LLCP? Equation (1) indicates that reducing the charges makes the Si—O interaction less attractive and the Si—Si and O—O interactions less repulsive. Of these competing effects, the Si—Si is the weakest, because its distance is relatively large. The Si—O interaction is the strongest, and it plays a role analogous to the hydrogen bond in water. Consistent with Fig. 1, reducing the charge reduces the Si—O attraction, which causes an increase of the volume (decrease of the density) and an increase in diffusivity (i.e., the glass transition moves to lower T).

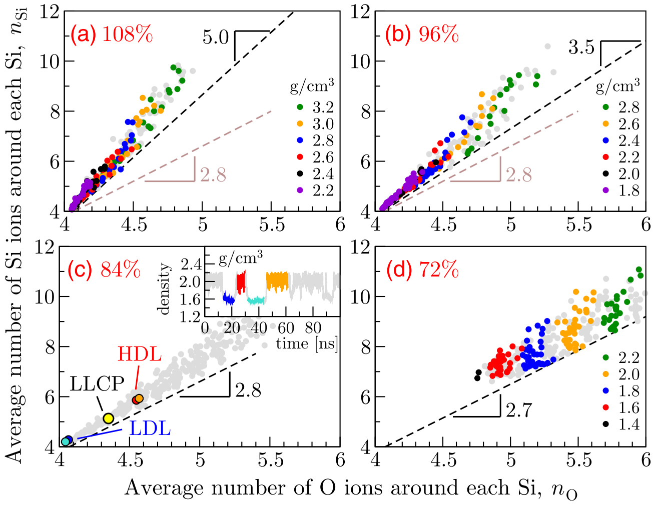

FIG. 2. Correlation between coordination numbers n_{Si} and n_{O}, for different values of the ion charge. Colors match those of the isochores in Fig. 1. At low T, the liquid prefers the tetrahedral LDL state, surrounded by $n_{\mathrm{O}} \approx 4$ O ions and $n_{\mathrm{Si}} \approx 4$ Si ions (lower-left corner in each panel). (a),(b) Increasing T or P increases the number of both O ions and Si ions. However, for each additional O ion, there is a minimum number of additional Si ions, as indicated by the black dashed line in each panel. (c) The slope of this line goes down as the charge is reduced, until it goes below ~3.5 Si/O and a LLCP appears. For $f_q = 0.84$, at (3240 K, 0.30 GPa) the liquid is exactly on the LLPT line and flips continuously between LDL (blue, turquoise) and HDL (red, orange); see the inset. We find that, for a LLCP to occur, the HDL phase must have a Si/O coordination number ratio below the 3.5 Si/O line. (d) Reducing the charge further makes the LLCP disappear below the liquid-vapor spinodal.

The competition between the strength of the Si—O bond and the Si—Si bond becomes clear when we compare the number of neighbors surrounding each Si ion. The coordination number n_{O} is the average number of O ions surrounding one Si and is defined by

$$n_{\mathrm{O}} \equiv 4\pi\rho_{\mathrm{O}} \int_0^{r_{\min}} r^2 g_{\mathrm{SiO}}(r) dr, \tag{2}$$

where ρ_{O} is the number density of the O ions, $g_{\mathrm{SiO}}(r)$ is the Si—O radial distribution function, and $r_{\min}$ is the location of its first minimum. In the same way, we use $g_{\mathrm{SiSi}}(r)$ and ρ_{Si} to define the coordination number n_{Si} as the average number of Si ions around one Si ion.

Figure 2 shows how the O coordination number correlates with the Si coordination number. Silica is a tetrahedral liquid, and therefore at low T the Si ions tend to configure with four Si neighbors. Because of the Coulomb repulsion, exactly four O ions are required to act as a “glue” between the Si ions. Hence, at low T we typically find the liquid near the $(n_{\mathrm{O}}, n_{\mathrm{Si}}) = (4, 4)$ state, i.e., the lower-left corner of each panel in Fig. 2. If we increase the temperature or pressure, a fifth O ion will move in and produce an imbalance in the charge, which in turn will attract additional Si ions. Increasing T or P thus increases n_{O}, which leads to an increase in n_{Si}.

The black dashed lines in Fig. 2 represent the minimum number of Si ions that surround a cluster of one Si ion plus n_{O} O ions. The slope of this line depends strongly on the amount of charge that the ions carry. The case $f_q = 1.08$, shown in Fig. 2(a), has the most charge per ion and therefore has the largest number of additional Si ions per added O ion: at least 5.0 additional Si ions for each additional O ion (5.0 Si/O). A reduction in f_q reduces the number of additional Si ions per O ion, until below $f_q \approx 0.94$ suddenly a LLCP appears [yellow circle in Fig. 2(c)]. Below $f_q \approx 0.78$, the liquid-vapor spinodal prevents the formation of a (meta)stable tetrahedral liquid state (LDL), and the LLCP disappears below the spinodal [Fig. 2(d)].

In Fig. 2(c), we focus on the state point (3240 K, 0.3 GPa) which lies near the LLCP and on the liquid-liquid phase transition line. This is clearly demonstrated by the "phase flipping" [28,29] between LDL and HDL that becomes visible when we plot how the density changes with time [see the inset in Fig. 2(c)]. Simulations at this state point allow us to compare the properties of the LDL and HDL phases. As expected, the coordination numbers of LDL lie close to (4,4), indicating that the liquid is strongly tetrahedral. The HDL coordination numbers lie on the opposite side of the LLCP, near $(n_{\mathrm{O}}, n_{\mathrm{Si}}) = (4.6, 6)$, indicating that the average Si ion in HDL is surrounded by 0.6 additional O ions that attract two additional Si ions. Note that the LLCP lies between the LDL and HDL points and is the average of the two phases.

Figure 2 suggests that a LLCP is possible only if the HDL has a Si coordination number below approximately 3.5 Si/O. Why the coordination number of HDL matters can be explained using the Gibbs free energy of mixing, $\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$. We may view the liquid as a mixture of LDL and HDL with their ratio controlled by a thermodynamic equilibrium, as has been done for water [30–33]. If $\Delta G_{\mathrm{mix}} > 0$, the LDL and HDL will spontaneously phase separate, and we may witness a liquid-liquid phase transition. But if the entropy of mixing ΔS_{mix} is large enough, $\Delta G_{\mathrm{mix}} < 0$ for all temperatures and pressures, and the liquid will remain homogeneous. This view together with the results of Fig. 2 seems to suggest that increasing the charges makes the Si─O bond stronger, causing a Si ion to draw more Si neighbors into the first coordination shell. This then leads to a relative increase in entropy of the HDL state and an increase of ΔS_{mix}, with the result that ΔG_{mix} becomes negative for all T and P if the ion charge is made large enough. A decrease in the ion charge reverses this effect and allows a liquid-liquid transition to appear.

It is important to emphasize that the LLCP is not driven by a demixing into two phases of different densities and different compositions, as might happen in a simple binary mixture [34,35]. The ions in this model carry a fixed charge, and they will therefore always appear in a Si∶O ratio of 1∶2, making a difference in composition impossible. Instead, the LDL and HDL phases differ in density and *structure*, analogous to what has been found for the LLCP in some models of water and silicon.

Because of great difficulty in estimating the melting line, it is unclear if the two liquid phases are stable or metastable. Unsurprisingly, a model for silica is an excellent glass former, and the liquid vitrifies long before crystallization can be witnessed [20]. Nonetheless, based on a visual inspection of trajectory snapshots as well as the phase flipping shown in the inset in Fig. 2(c), it seems clear that the model shows a liquid-liquid transition rather than liquid-solid.

Values such as the 3.5 Si/O are only approximate; they are sensitive to the criteria used to calculate the coordination numbers (see Supplemental Material [36]) and are likely to depend on the parameters of the model. We can generalize these ideas, however, by comparing our results to the idea of "potential softness" [37]. A potential that is too soft will have too many neighbors per atom in the HDL phase, leading to an increased entropy of mixing, thus possibly preventing a transition between LDL and HDL if the Gibbs free energy of mixing becomes negative for all T and P. Here we adjust the softness by changing the Si─O strength (via the ion charge), but it is likely that similar findings can be obtained by careful adjustment of the van der Waals parameters A_{ij} and B_{ij}.

In conclusion, we have shown in this Letter that it is possible for a model to be tuned such that it smoothly transitions from having a LLCP to not having a LLCP and in a manner different from moving the LLCP below a spinodal or glass transition line (which, for instance, can be done by making bond angles more flexible [38] or less tetrahedral [39]). This means that it is theoretically possible to observe response function behaviors in a real liquid at high temperatures that seem to indicate the presence of a LLCP when a LLCP is not actually there but that nevertheless the system is "close" to having one (as in the case of $f_q \geq 0.96$). It is therefore important to study a liquid at multiple pressures to check that there are no separated global response function maxima. Note that in the case of water there is experimental evidence that strongly supports the existence of a LLCP, such as the first-order-like transition between amorphous ices LDA and HDA [40–42] which would not show hysteresis if water were only close to having a LLCP.

Finally, this model also presents a possible experimental method of validating the existence of LLCPs using charged colloids [43]. Although experiments using colloids with tetrahedral bonds have already been suggested [37], our work indicates that a LLCP could also be obtained by creating a liquid mixture of charged colloids, with the charge carefully calibrated.

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