

## Comparison of Thermodynamic Properties of Simulated Liquid Silica and Water

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We conduct extensive molecular dynamics computer simulations of a rigid-ion model of liquid silica [L.V. Woodcock *et al.*, J. Chem. Phys. **65**, 1565 (1976)], evaluating thermodynamic and transport properties over a wide range of pressure and temperature. We find numerous similarities with behavior found in simulations of supercooled water, including a line of density maxima that passes through a maximum temperature as a function of pressure, and the emergence as temperature decreases of maxima in isotherms of the isothermal compressibility as a function of density. [S0031-9007(97)04109-4]

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There has been considerable recent interest in the low temperature thermodynamic properties of liquids—especially water—in which the local molecular structure is dominated under ambient pressure by tetrahedral arrangements of molecules [1]. In particular, molecular dynamics (MD) simulations [2] have been used to evaluate the properties of liquid water over a wide range of temperature  $T$  and pressure  $P$ . Such studies qualitatively reproduce the observed thermodynamic properties of water, including the well-known occurrence of a maximum in the density  $\rho$  as a function of  $T$  at constant  $P$  [3].

Simulations have also found new behaviors that have not yet been verified experimentally due to the difficult thermodynamic conditions under which they are predicted to occur [4,5]. For example, the locus of points at which density maxima occur—the temperature of maximum density (TMD) line—is negatively sloped in the  $P$ - $T$  plane for  $P > 0$  [3]. However, simulations predict that for  $P < 0$  the TMD line reaches a maximum  $T$  and becomes positively sloped. Also, at low  $T$  simulations predict that maxima appear in the isothermal compressibility  $\kappa_T$  as a function of  $\rho$  at constant  $T$ . These new behaviors have been found in simulations of several water interaction potentials, including ST2 [6] and TIP4P [7]. In the case of ST2 the  $\kappa_T$  maxima evolve as  $T$  decreases into a critical point and line of first-order liquid-liquid phase transitions [8]. Though it has yet to be determined experimentally if this phase transition occurs in water, its existence would be relevant for understanding the amorphous solid state of water. Experimental studies have established the existence of distinct high and low density forms of vitreous water at low  $T$  [9], a phenomenon termed “polyamorphism” [10]. It has been proposed that the polyamorphism of amorphous solid water is a manifestation in the glassy regime of a liquid-liquid phase transition [4].

It has long been appreciated [11] that liquid silica ( $\text{SiO}_2$ ), having also a local tetrahedral structure, is similar to water. Silica exhibits a density maximum in the liquid phase, as well as polyamorphism in the glassy state [12], though less dramatically than for water. It is not presently known, either experimentally or through simulation, if

the thermodynamic behavior predicted in simulations of supercooled water might apply to liquid silica. In this Letter, we present the results of extensive MD simulations of a rigid-ion model [13] of liquid silica to test for the occurrence of behavior of the type found in simulations of water.

The behavior found in simulations of supercooled water, such as a maximum in  $\kappa_T$ , occurs for  $T$  well below that of the TMD line [4,14]. To test for similar behavior in simulations of silica, we require a silica interaction potential that both exhibits a density maximum and also permits simulation of the equilibrium liquid over a wide range of lower  $T$ . These requirements are met by the rigid-ion model of silica developed by Woodcock *et al.* [13,15]. The density maximum of this model [16] can be located by evaluating  $P(\rho, T)$ , the equation of state of the equilibrium liquid. Minima in isochores of  $P$  versus  $T$  identify points on the TMD line (Fig. 1). The TMD line for the model occurs at  $T$  much higher than that observed experimentally in silica at 1823 K [11]. This discrepancy reflects the approximate nature of the model, which neglects certain

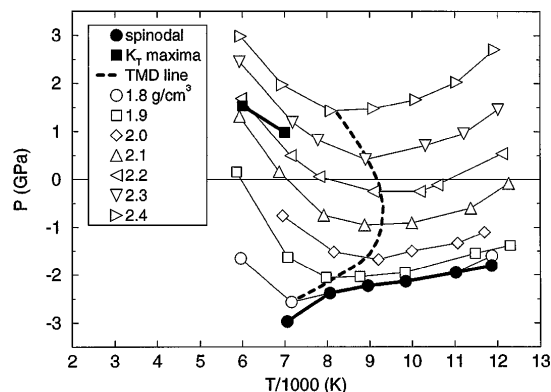


FIG. 1. Isochores of  $P$  versus  $T$  for  $\rho$  from 1.8 to 2.4  $\text{g}/\text{cm}^3$ . The TMD line is the line joining the minima of the isochores. The liquid spinodal is estimated as the lowest value of  $P$  observed along each  $P$ - $\rho$  isotherm shown in Fig. 3. The position of the line of  $\kappa_T$  maxima is determined from the states at which the maxima occur in Fig. 4.

features of the interionic interactions in silica (e.g., ion polarizability). From a computational standpoint, the glass transition temperature,  $T_g$ —the  $T$  at which equilibrium cannot be established within our maximum run time of 1 ns—occurs for this model at approximately 5000 K at ambient  $P$ . However, the shift of the TMD line to higher  $T$  places the TMD line in a highly fluid regime where  $T \gg T_g$ . As shown in Fig. 2, the diffusion coefficient  $D$  remains large enough to permit equilibrium simulations over a range of 3000 K below the TMD line.

The present model reproduces the structure of silica liquid and glass reasonably well [13]; however, overall it is found to underestimate the long-range order of the tetrahedral network. Other models, especially those incorporating three-body effects or ion polarizability, clearly are more accurate [17]. On the other hand, this model remains the best of many for reproducing the ion mobilities, and hence the value of  $D$ , for liquid silica [18]. (In this regard, the occurrence in Fig. 2 of maxima along isotherms of  $D$  versus  $\rho$  is significant. This substantial dynamic anomaly has been noted in previous simulations of liquid silica [19], and is experimentally observed in both silicates [20] and water [21].) For the present purpose, this silica model is useful because, being a simple two-body potential, it permits more efficient simulation of the many state points and long time scales required, compared to more complex potentials. It is also the only model that presently affords the opportunity to explore the behavior of a silicalike liquid for  $T$  less than the TMD; in simulations of other silica models, the TMD line recedes to much lower  $T$  [18,22]. However, given the shortcomings of the model, in the following we restrict our attention to only the qualitative implications of our results.

We evaluate  $P$  and  $U$ , the configurational part of the internal energy, as a function of  $\rho$  and  $T$ . We find that the present model exhibits many of the thermodynamic behaviors found in simulations of supercooled water:

(i) The TMD line found in our silica simulations (Fig. 1) has a negative slope for  $P > 0$ , similar to laboratory [3] and simulated water [4]. However, the

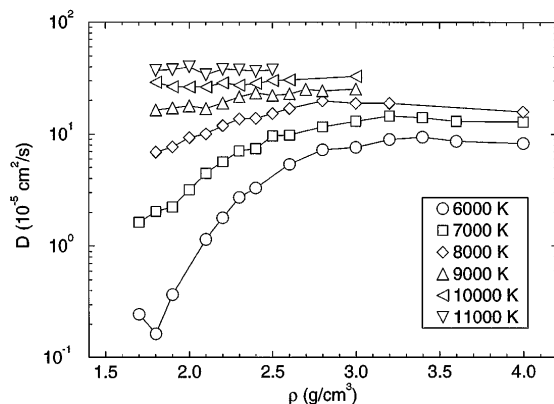


FIG. 2. Isotherms of the diffusion coefficient  $D$  of O ions as a function of  $\rho$ .

present results allow us to determine the shape of the TMD line as it extends into the metastable region for  $P < 0$ . We find, as in simulated water [4], that the sign of the slope reverses, becoming positive for  $P < 0$ .

(ii) We also locate points on the liquid spinodal, the boundary at negative  $P$  at which the liquid cavitates due to hydrostatic tensile stress (Fig. 1). Of particular interest in the study of water is the question of whether the liquid spinodal is reentrant to positive  $P$ , a behavior that can occur if the spinodal and TMD lines intersect [23]. Our results for liquid silica are qualitatively identical to those found for simulated water [compare with Fig. 2(c) of the first reference given in [4]]: in both water and silica simulations, the spinodal and TMD lines do not intersect, precluding the possibility of a reentrant spinodal for both of these liquid models.

(iii) Simulations of supercooled water predict that a maximum occurs in  $\kappa_T$  as a function of  $\rho$  at constant  $T$  [4]. We address the question of a  $\kappa_T$  maximum in the present model by examining isotherms of  $P$  versus  $\rho$ , plotted in Fig. 3. For  $T = 9000$  K,  $P$  varies with  $\rho$  in a manner typical of a simple liquid. However, at  $T = 7000$  and  $6000$  K the isotherms begin to flatten over an interval of  $\rho$  near  $2.2$  g/cm<sup>3</sup>, an effect which becomes more pronounced as  $T$  decreases. We evaluate  $\kappa_T$  from the relation  $\kappa_T = (1/\rho)(\partial\rho/\partial P)_T$ , and indeed find that a maximum appears in  $\kappa_T$  as  $T$  decreases (Fig. 4), generating a line of  $\kappa_T$  maxima in the  $P$ - $T$  plane (Fig. 1). As in water simulations [4], we find that the magnitude of  $\kappa_T$  along the line of  $\kappa_T$  maxima increases as  $T$  decreases; and, that the line of  $\kappa_T$  maxima is negatively sloped in the  $P$ - $T$  plane.

(iv) We present the behavior of isotherms of  $U$  as a function of volume  $V = 1/\rho$  in Fig. 5. For the present silica model at the highest  $T$ , an isotherm of  $U$  is a concave-upward function of  $V$ . However, as  $T$  decreases, the value of the curvature  $(\partial^2 U/\partial V^2)_T$  decreases, even converting to slightly negative curvature over a substantial range of  $V$  at the lowest  $T$ . Thermodynamic stability requires that  $(\partial^2 A/\partial V^2)_T > 0$ , where  $A$  is the Helmholtz

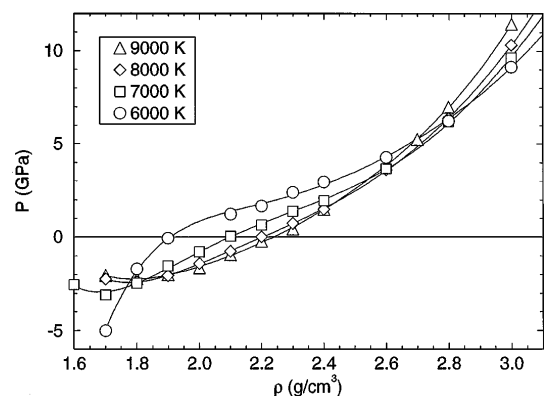


FIG. 3. Isotherms of  $P$  as a function of  $\rho$ . The solid lines are fits of the data to a sixth-order polynomial.

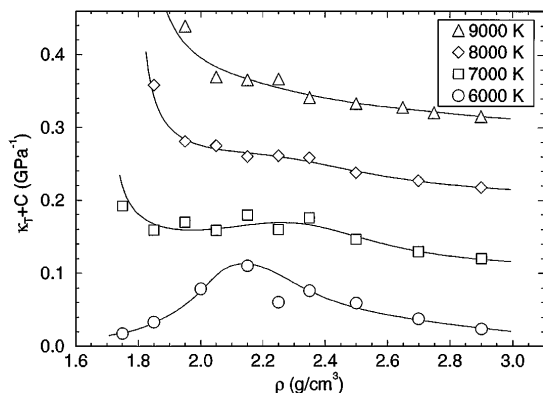


FIG. 4. Isotherms of  $\kappa_T$  as a function of  $\rho$  calculated using the derivative of the polynomial fits in Fig. 3 (solid lines), and using the piecewise slope of the  $P$ - $\rho$  data in Fig. 3 (symbols).  $C$  is a shift parameter to facilitate comparison of the curves;  $C = (T - 6000 \text{ K})/(10^4 \text{ K GPa})$ .

free energy. From standard thermodynamic relations,  $(\partial^2 A / \partial V^2)_T = (\partial^2 U / \partial V^2)_T - T(\partial^2 S / \partial V^2)_T$ , where  $S$  is the entropy. Hence the effect of  $(\partial^2 U / \partial V^2)_T$  is to progressively *lower* the stability of the liquid over a range of  $V$  as  $T$  decreases, an effect consistent with the appearance and growth of the  $\kappa_T$  maxima obtained from the  $P$  versus  $\rho$  data. Moreover, this behavior for  $U$  is also observed in simulations [4] of water.

(v) Figure 6 shows the experimental dependence of  $P$  on  $\rho$  during shock compression of fused silica [12]. Here the characteristic signature of polyamorphism is observed as an interval of flattening over which  $\rho$  increases substantially over a small range of  $P$ . This corresponds to a  $\kappa_T$  maximum in the glass. Abrupt densification of silica glass is known to be reproduced in simulations [24]. We too find abrupt densification of the glass when using the same silica interaction potential and computational protocol used here to study the liquid state (Fig. 6) [25]. This test establishes that, as in water simulations, a  $\kappa_T$  maximum is found for both the glass and equilibrium liquid in simulations of the same silica model.

Because of the rapidly increasing liquid relaxation time as  $T$  decreases, we are not able to conduct simulations of

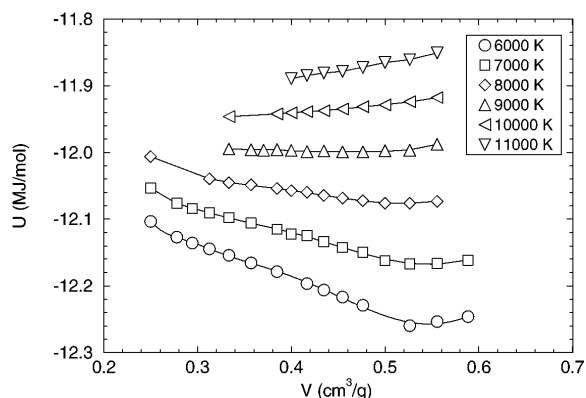


FIG. 5. Isotherms of  $U$  as a function of  $V$ . The solid lines are fits of the data to a sixth-order polynomial.

the equilibrium liquid at  $T$  low enough to test directly if a liquid-liquid phase transition occurs in this silica model, as occurs in the ST2 model of water. A liquid-liquid phase transition has been proposed to occur not only for water [4], but also for other tetrahedral liquids such as Ge [26] and C [27], and has been directly observed for a lattice model of a tetrahedral liquid [28]. In the case of Si, an amorphous solid to liquid transition has been observed experimentally [29], and also in simulations of the Stillinger-Weber potential for Si [30,31]. Although other interpretations of this phenomenon exist [32], it might also be understood in terms of an underlying liquid-liquid transition. The present results suggest that silicalike liquids, and hence perhaps real silica, are also candidates to exhibit a liquid-liquid transition. However, given the approximate nature of the present model, both high- $T$  experiments on liquid silica, and extensive simulations of more realistic silica models are required to determine the applicability of the present results to real silica.

In summary, we find for the silica model of Ref. [13] the same pattern of thermodynamic behavior as that found from simulations of water. This similarity exists despite the differences between the interaction potentials for silica and water. The present silica potential consists of unconstrained spherical ions which generate tetrahedral arrangements through local charge balance and stoichiometry. The simulation results for water were obtained using rigid molecular models in which tetrahedral coordination is achieved via a fixed near-tetrahedral H-O-H angle. Our results therefore support the possibility that a “law of corresponding states” applies to the thermodynamic properties of many tetrahedral liquids, irrespective of the microscopic details of the intermolecular interaction.

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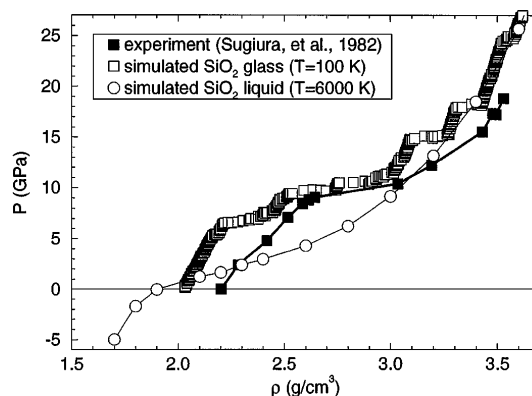


FIG. 6. Comparison of simulated and experimental results of  $P$  versus  $\rho$  for shock compression of silica glass. The experimental results are those of Ref. [12] for fused silica. For comparison, the liquid state data for  $T = 6000 \text{ K}$  from Fig. 3 are also shown.

- [1] P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, 1997); C. A. Angell, *Science* **267**, 1924 (1995).
- [2] M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids* (Oxford University Press, Oxford, 1987).
- [3] A. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University Press, London, 1969).
- [4] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, *Nature* (London) **360**, 324 (1992); *Phys. Rev. E* **48**, 3799 (1993); P. H. Poole, U. Essmann, F. Sciortino, and H. E. Stanley, *Phys. Rev. E* **48**, 4605 (1993); F. Sciortino, P. H. Poole, U. Essmann, and H. E. Stanley, *Phys. Rev. E* **55**, 727 (1997).
- [5] H. Tanaka, *Nature* (London) **380**, 328 (1996).
- [6] F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **60**, 1545 (1974).
- [7] W. L. Jorgensen, J. Chandrasekhar, J. Madura, R. W. Impey, and M. Klein, *J. Chem. Phys.* **79**, 926 (1983).
- [8] S. Harrington, R. Zhang, P. H. Poole, F. Sciortino, and H. E. Stanley, *Phys. Rev. Lett.* **78**, 2409 (1997).
- [9] O. Mishima, L. D. Calvert, and E. Whalley, *Nature* (London) **314**, 76 (1985); O. Mishima, *J. Chem. Phys.* **100**, 5910 (1994).
- [10] G. H. Wolf *et al.*, in *High-Pressure Research: Application to Earth and Planetary Sciences*, edited by Y. S. Manghni and M. H. Manghni (American Geophysical Union, Washington, 1992), p. 503; P. H. Poole, T. Grande, C. A. Angell, and P. F. McMillan, *Science* **275**, 322 (1997).
- [11] C. A. Angell and H. Kanno, *Science* **193**, 1121 (1976); C. A. Angell, P. A. Cheeseman, and S. Tamaddam, *Science* **218**, 885 (1982).
- [12] H. Sugiura, K.-I. Kondo, and A. Sawaoka, in *High-Pressure Research in Geophysics*, edited by S. Akimoto and M. H. Manghni (Reidel, Dordrecht, 1982), p. 551; M. Grimsditch, *Phys. Rev. Lett.* **52**, 2379 (1984).
- [13] L. V. Woodcock, C. A. Angell, and P. A. Cheeseman, *J. Chem. Phys.* **65**, 1565 (1976).
- [14] S. Sastry, P. G. Debenedetti, F. Sciortino, and H. E. Stanley, *Phys. Rev. E* **53**, 6144 (1996).
- [15] The simulated liquid consists of oxygenlike and siliconlike ions which interact via a pairwise additive interaction potential consisting of a Coulombic interaction and a short-range repulsive term of the Born-Mayer-Huggins form. Our simulations consist of  $N = 450$  ions (300 oxygen and 150 silicon ions) enclosed in a cubic simulation cell employing periodic boundary conditions. Short-range interactions are truncated at half the length of the simulation cell, while the method of Ewald summation is used to account for the long-range nature of the Coulomb interactions. The time step used for integrating the equations of motion is 2 fs. Equilibrated liquid state configurations are generated by first constraining  $T$  near a desired value by periodic rescaling of the particle velocities, followed by an extended evolution of the system without velocity rescaling, to bring the liquid into equilibrium in the microcanonical ensemble ( $N$ ,  $\rho$ , and total energy  $E$  held constant). Equilibration and production run times vary widely, depending on the thermodynamic state. The equilibration phase is deemed complete when bulk properties such as  $U$  and  $P$  have reached a steady state, and when the mean square displacement of the ions is found to scale linearly with time  $t$  over at least one decade of  $t$ . A production phase is then initiated for the evaluation of the liquid state properties  $T$ ,  $P$ ,  $U$ , and  $D$ . Because our data are generated from runs in the microcanonical ensemble the final average  $T$  for each state point will vary slightly from the desired "target" value. To construct isothermal curves from our data we estimate the value of the desired property from a linear interpolation between two nearby states of the same  $\rho$ , at  $T$  higher and lower than the desired  $T$ .
- [16] D. R. Perchak and J. M. O'Reilly, *J. Non-Cryst. Solids* **167**, 211 (1994).
- [17] See, for example, S. Tsuneyuki *et al.*, *Phys. Rev. Lett.* **61**, 869 (1988); B. W. H. van Beest *et al.*, *Phys. Rev. Lett.* **64**, 1955 (1990); P. A. Vashista *et al.*, *Phys. Rev. B* **41**, 12 197 (1990); M. Wilson *et al.*, *Phys. Rev. Lett.* **77**, 4023 (1996).
- [18] M. Hemmati and C. A. Angell (unpublished).
- [19] C. A. Angell, P. Cheeseman, and S. Tamaddam, *Bull. Mineral.* **106**, 87 (1983).
- [20] I. Kushiro, *Geochim. Cosmochim. Acta* **47**, 1415 (1983).
- [21] F. X. Prielmeier *et al.*, *Phys. Rev. Lett.* **59**, 1128 (1987).
- [22] K. Vollmayr, W. Kob, and K. Binder, *Phys. Rev. B* **54**, 15 808 (1996).
- [23] R. J. Speedy and C. A. Angell, *J. Chem. Phys.* **65**, 851 (1976); P. G. Debenedetti and M. C. D'Antonio, *J. Chem. Phys.* **84**, 3339 (1986).
- [24] M. S. Somayazulu *et al.*, *J. Phys. Condens. Matter* **5**, 6345 (1993); J. S. Tse, D. D. Klug, and Y. LePage, *Phys. Rev. B* **46**, 5933–5938 (1992); W. Jin, R. K. Kalia, and P. Vashishta, *Phys. Rev. Lett.* **71**, 3146 (1993).
- [25] To simulate the compression of silica glass, first a liquid state configuration at  $T = 7000$  K and  $\rho = 2.0$  g/cm<sup>3</sup> is equilibrated and then quenched into an amorphous solid by linearly decreasing  $T$  to 100 K over 100 ps. This configuration is then used to initiate a compression run during which  $T$  is constrained near 100 K using periodic velocity rescaling. Compression is simulated by controlling  $P$  using the method of Parrinello and Rahman [33]. Starting from the initial value of  $P$  measured for the quenched configuration,  $P$  is increased linearly over the course of the run at the rate of 0.125 GPa/ps. The small stepwise changes observed during compression occur as localized groups of atoms reorganize as  $\rho$  increases.
- [26] E. G. Ponyatovsky and O. I. Barkalov, *Mater. Sci. Rep.* **8**, 147 (1992).
- [27] M. van Thiel and F. H. Ree, *Phys. Rev. B* **48**, 3591 (1993).
- [28] C. J. Roberts, A. Z. Pangiotopoulos, and P. G. Debenedetti, *Phys. Rev. Lett.* **77**, 4386 (1996).
- [29] M. O. Thompson *et al.*, *Phys. Rev. Lett.* **52**, 2360 (1984); E. P. Donovan *et al.*, *J. Appl. Phys.* **57**, 1795 (1985).
- [30] F. H. Stillinger and T. Weber, *Phys. Rev. B* **31**, 5262 (1985).
- [31] W. D. Ludke and U. Landman, *Phys. Rev. B* **37**, 4656 (1988); C. A. Angell, S. Borick, and M. Grabow, *J. Non-Cryst. Solids* **205-207**, 463 (1996).
- [32] F. H. Stillinger, *Physica* (Amsterdam) **177A**, 97 (1991).
- [33] M. Parrinello and A. Rahman, *J. Appl. Phys.* **52**, 7182 (1981).