

## LETTER TO THE EDITOR

**Density minimum and liquid–liquid phase transition****Peter H Poole<sup>1</sup>, Ivan Saika-Voivod<sup>2,3</sup> and Francesco Sciortino<sup>2</sup>**<sup>1</sup> Department of Physics, St Francis Xavier University, Antigonish, NS, B2G 2W5, Canada<sup>2</sup> Dipartimento di Fisica and INFN-CRS-Soft, Università di Roma La Sapienza, Piazzale Aldo Moro 2, I-00185, Roma, Italy<sup>3</sup> Department of Chemistry, University of Saskatchewan, Saskatoon, SK, S7N 5C9, Canada

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Online at [stacks.iop.org/JPhysCM/17/L431](http://stacks.iop.org/JPhysCM/17/L431)**Abstract**

We present a high-resolution computer simulation study of the equation of state of ST2 water, evaluating the liquid-state properties at 2718 state points, and precisely locating the liquid–liquid critical point (LLCP) occurring in this model. We are thereby able to reveal the interconnected set of density anomalies, spinodal instabilities and response function extrema that occur in the vicinity of an LLCP for the case of a realistic, off-lattice model of a liquid with local tetrahedral order. In particular, we unambiguously identify a density minimum in the liquid state, define its relationship to other anomalies, and show that it arises due to the approach of the liquid structure to a defect-free random tetrahedral network of hydrogen bonds.

(Some figures in this article are in colour only in the electronic version)

Water is not only the most abundant liquid on earth, but also a prototype of many network forming materials. As for water, important substances such as silicon and silica exhibit in their liquid phase a disordered network structure that arises due to highly directional tetrahedral bonding interactions. It has long been appreciated that the development of an open tetrahedral network on cooling is related to the occurrence of the density maximum observed in these liquids [1]. In water the density maximum occurs at 277 K at ambient pressure  $P$ . For temperatures  $T$  above the density maximum, the isobaric expansivity  $\alpha_P$  is positive, as for the vast majority of liquids. As  $T$  decreases through the density maximum,  $\alpha_P$  decreases to zero and then becomes negative; in this region the liquid expands on cooling. For all liquids with density maxima, an open question concerns what happens as  $T$  decreases further: does  $\alpha_P$  remain negative, or eventually return to ‘normal’ positive values? In the latter case, the  $T$  at which  $\alpha_P$  again becomes positive corresponds to a density minimum.

A density maximum, although well known in the case of water, occurs in only a few liquids. Experimental observations of liquid-state density minima are almost non-existent; we have found only one report in the literature, a study of a mixture of Ge and Se [2]. Yet the possibility of a density minimum occurring in deeply supercooled water and similar systems

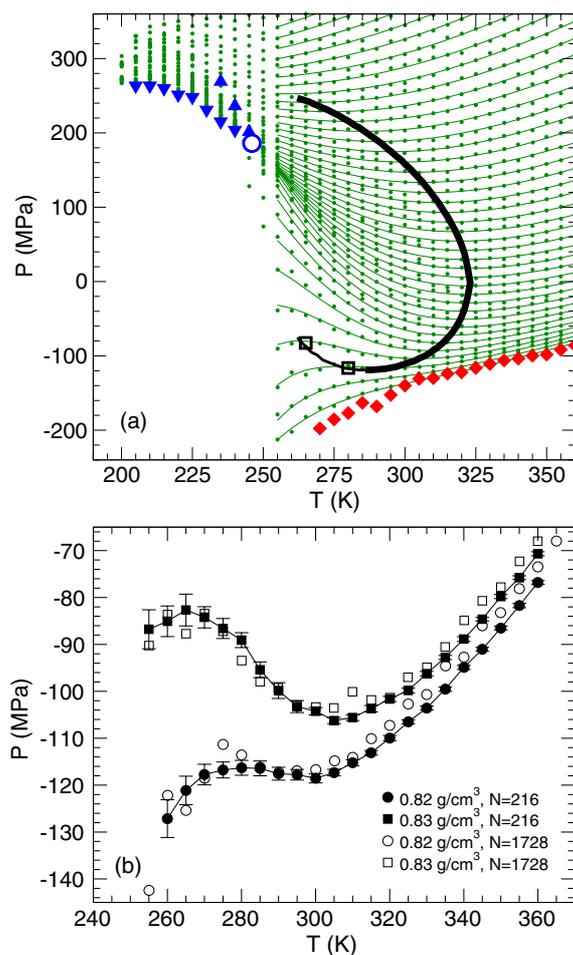
has been discussed in the literature (see e.g. [3]), and is supported by several theoretical and simulation studies. Density minima have been identified in lattice models of network-forming fluids [4], and recent computer simulations of water [5–7] also present data in which a liquid-state density minimum, or a trend toward one, is seen or can be inferred. Also notable is the recent experimental report of a density minimum in vitreous silica, although non-equilibrium effects complicate the interpretation of the results in terms of equilibrium liquid-state behaviour [8].

At the same time, a growing body of evidence suggests that a liquid–liquid critical point (LLCP) may also be a characteristic feature of liquids with local tetrahedral order [9–13]. Below such an LLCP, two distinct liquid phases, the so-called ‘low density’ and ‘high density’ liquids (respectively LDL and HDL), are separated by a line of first order phase transitions. Formal thermodynamic analysis has revealed general relationships that must be satisfied in a liquid displaying both density anomalies and the anomalies associated with an LLCP [14, 4, 15–18]. Some studies, such as in [8], associate multiple density anomalies with a polyamorphic transition related to an LLCP. However, an unambiguous realization of these relationships for a realistic, off-lattice, equilibrium molecular liquid has not been reported, either experimentally or in computer simulations, in particular, the implications of a liquid-state density minimum merit focused study, both in terms of its relationship to the LLCP, as well as understanding its origins in terms of the low  $T$  thermodynamic and structural behaviour of the liquid. For example, if a density maximum is followed at lower  $T$  by a density minimum, it means that many, if not all of the anomalies for which water in particular is famous, ultimately disappear under sufficient supercooling. The possibility of such a return to ‘normal’ behaviour has important implications for understanding the properties of bulk supercooled water, the amorphous ices, as well as composite systems in which the tetrahedral network is influenced by surfaces or solutes [5, 7].

In this letter, we present a high-resolution computer simulation study of the equation of state (EOS) of ST2 water [21], a molecular dynamics model known to exhibit a prominent density maximum and also a clear example of an LLCP [9]. As shown below, we find in addition that this model liquid displays a density minimum. We are thereby able to reveal the thermodynamic context in which this density minimum occurs, identify the structural origins of the anomaly, and clarify its relationship to the LLCP.

Our results are based on molecular dynamics simulations of liquid systems of  $N = 1728$  molecules. All simulations are carried out at constant  $N$  and volume  $V$ , and  $T$  is maintained at the desired value using Berendsen’s method [22] with a time constant for the relaxation of  $T$  fluctuations of 2 ps. Molecular interactions are cut off at a distance of 0.78 nm, and the reaction field method is used to approximate the contribution of dipole–dipole interactions at longer range. The time step used is 1 fs.

Our simulation protocol is as follows: randomized starting configurations are prepared at each density  $\rho$  to be studied and are used to initiate runs at 400 K. An equilibration and a production phase are carried out, after which the target  $T$  is reduced by 5 K, and a new equilibration/production cycle is initiated using the last configuration of the previous run. In this way, the properties of successive state points along the specified isochore (i.e. at constant  $\rho$ ) are evaluated with decreasing  $T$ . Both the equilibration and production phases at each  $T$  are carried out for the time required for the mean squared displacement (MSD) to reach  $1 \text{ nm}^2$ , or for 100 ps, whichever is larger. Note that a MSD of  $1 \text{ nm}^2$  corresponds to an average displacement of about 3 times the distance between nearest neighbour molecules in liquid water at  $\rho = 1.0 \text{ g cm}^{-3}$ . For our lowest  $T$  state points, our run-time criterion leads to simulations of on the order of 100 ns. Using the above protocol, we evaluate the properties of the liquid at 2718 state points: at densities from  $\rho = 0.70$  to  $1.50 \text{ g cm}^{-3}$  in steps of  $0.01 \text{ g cm}^{-3}$ ; and for



**Figure 1.** (a) Phase diagram of the ST2 liquid, evaluated from MD simulations of a system of 1728 molecules. State points simulated are shown as small dots. Isochores (thin lines through dots) obtained from our fitted EOS are shown from  $\rho = 0.80 \text{ g cm}^{-3}$  (bottom-most line) and greater in steps of  $0.01 \text{ g cm}^{-3}$ . Also shown is the estimated location of the liquid–gas spinodal (diamonds), the LDL spinodal (up-triangles), the HDL spinodal (down-triangles), and the LLCP (circle).  $\Delta_{\max}$  (thick line) transforms into  $\Delta_{\min}$  (thin line) at low  $P$ . Squares locate points on  $\Delta_{\min}$  obtained from (b). (b) Variation of  $P$  with  $T$  along the  $\rho = 0.82$  and  $0.83 \text{ g cm}^{-3}$  isochores for both the  $N = 1728$  and  $216$  systems. For the  $N = 216$  data, error bars are drawn at twice the standard deviation of the means of  $P$  as evaluated from each of the 40 runs conducted at each state point.

$T$  from 400 K down to at least 255 K, in 5 K steps. Along some isochores, a  $T$  as low as 200 K is reached. The sum of the computational work reported here corresponds to approximately 30 cpu years on a 3.0 GHz Intel Xeon processor.

The resulting EOS data for  $P(\rho, T)$  is shown in figure 1(a). Early support for the possibility of an LLCP in water was based on the shape of the ST2 EOS reported in [9]. These features of the ST2 model are seen here in much greater detail. The LLCP is readily located, as well as the metastability limits (spinodals) of both the LDL and HDL phases that meet at the critical point. We also identify an upper bound on the location of the liquid–gas spinodal by locating the cavitation limit of the liquid at the extreme low  $\rho$  range at negative  $P$ .

Figure 1(a) shows most of the individual state points simulated, as well as isochores obtained from the fit of an analytic EOS to the data set<sup>4</sup>. Points on the locus of density maxima  $\Delta_{\max}$  are coincident with the minima of these isochores. As  $\rho$  decreases,  $\Delta_{\max}$  follows a retracing path in the  $T$ - $P$  plane to  $\rho = 0.82 \text{ g cm}^{-3}$ , but notably, the isochores for  $\rho = 0.81$  and  $0.80 \text{ g cm}^{-3}$  do not exhibit minima. Rigorous thermodynamic arguments have shown that  $\Delta_{\max}$  cannot end at finite  $T$  in isolation from other anomalies [14–16]. It must either terminate on a spinodal locus, or  $\Delta_{\max}$  itself must pass through an extremum in the  $T$ - $P$  plane, at which point it becomes a line of density minima,  $\Delta_{\min}$ . We find that the latter possibility occurs, as shown by both the shape of  $\Delta_{\max}$  and the EOS isochores: low  $T$  maxima in the  $\rho = 0.82$  and  $0.83 \text{ g cm}^{-3}$  isochores correspond to points on  $\Delta_{\min}$ .

To further confirm the existence of  $\Delta_{\min}$ , we conduct a new set of simulations focusing on the  $\rho = 0.82$  and  $0.83 \text{ g cm}^{-3}$  isochores, with the aim of reducing the statistical errors. These simulations employ a smaller system size,  $N = 216$ , but we average over an ensemble of 40 independent runs for each state point<sup>5</sup>. The variation of  $P$  with  $T$  along these two isochores (figure 1(b)) confirms that both a density maximum and a density minimum occur. The locations of the density minima so identified are shown as squares in figure 1(a), and are consistent with the predictions of the data set obtained using 1728 molecules.

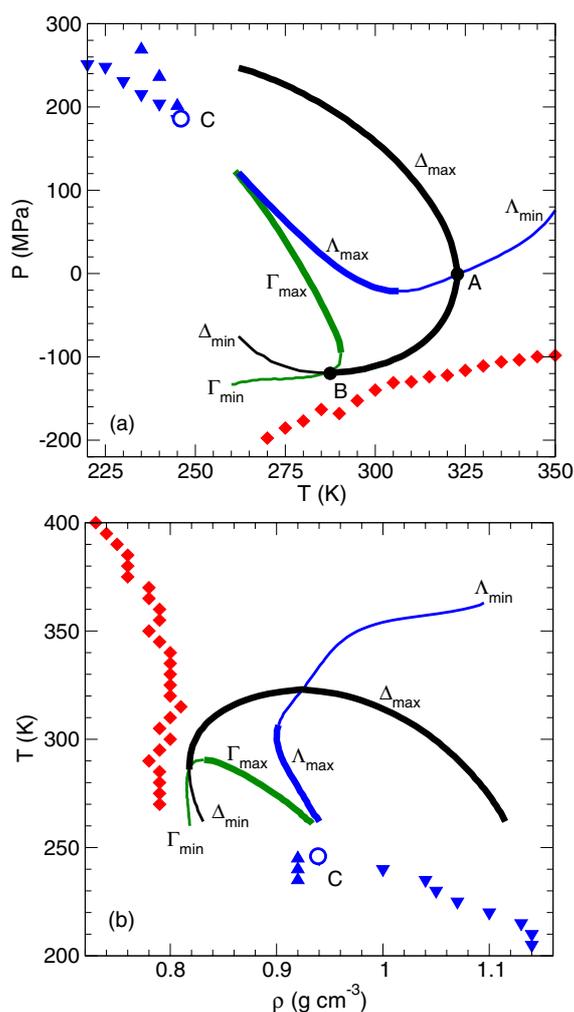
All along the locus  $\Delta$  (the union of  $\Delta_{\max}$  and  $\Delta_{\min}$ ) the condition  $(\partial\rho/\partial T)_P = 0$  is satisfied. Formal thermodynamic analysis has shown that changes of sign of the slope of  $\Delta$  in the  $T$ - $P$  plane are associated with intersections with certain response function extrema. Reference [17] shows that the point  $A$  in figure 2(a), where  $\Delta$  has infinite slope, is coincident with a point on a locus  $\Lambda$  along which  $(\partial K_T/\partial T)_P = 0$ , where  $K_T$  is the isothermal compressibility. By evaluating the appropriate derivative of our fitted EOS, we confirm that this requirement is satisfied. We also identify a new thermodynamic relation, derived by analogy to those in [17] and [18], that states that point  $B$  in figure 2(a), where  $\Delta$  has zero slope, is coincident with a point on a locus  $\Gamma$  along which  $(\partial C_P/\partial P)_T = 0$ , where  $C_P$  is the isobaric specific heat. This requirement is also satisfied by our fitted EOS. Figure 2(b) shows the location of the features of (a) in the  $\rho$ - $T$  plane.

At the same time, the curves  $\Lambda$  and  $\Gamma$  are formally related to the LLCPC. At an LLCPC, denoted  $C$ , isotherms of  $C_P$  and isobars of  $K_T$  will both exhibit a divergence. For  $T > T_C$ ,  $\Lambda$  and  $\Gamma$  radiate outward from  $C$  as lines of maxima that are the supercritical extension of the divergence occurring as  $T \rightarrow T_C$ . In the present data, these maxima transform into minima, and then intersect the line  $\Delta$ , controlling the sign of its slope. While the existence of these response function extrema is not a sufficient condition for there being an LLCPC at lower  $T$ , it is a necessary condition [17]. The interconnected pattern of density anomalies and response function extrema shown here therefore illustrates how the discovery of such features in experimental data can provide a rational procedure for locating an LLCPC at lower  $T$ .

Examination of the thermodynamics and structure of the liquid in the vicinity of the density minimum reveals why it occurs. As shown in figure 3, both the potential energy  $U$ , and the fraction of network defects  $f_d$  [19, 20], are at the lowest  $T$  behaving more and more as they would for a system approaching a random tetrahedral network (RTN) in which all

<sup>4</sup> We create a fitted EOS model of the data for  $P(V, T)$  and  $E(V, T)$  for  $255 \text{ K} \leq T \leq 400 \text{ K}$  and  $0.80 \text{ g cm}^{-3} \leq \rho \leq 1.30 \text{ g cm}^{-3}$ , where  $E$  is the total energy. This encompasses 1530 state points. To model both the  $P(V, T)$  and  $E(V, T)$  data, we carry out a least-squares fit to a bivariate polynomial of the form  $\sum_{i=0}^7 \sum_{j=0}^6 a_{ij} c_i(V) c_j(T)$  where  $c_i(V)$  is the Chebyshev polynomial of the first kind of degree  $i$  as a function of  $V$ ,  $c_j(T)$  is similarly defined, and the  $a_{ij}$  are the fit parameters. Extrema of  $\rho$  and  $K_T$  are found from the fit to the  $P(V, T)$  data. Extrema of  $C_P$  are found by isobarically differentiating the enthalpy  $H(P, T) = E + PV$ .

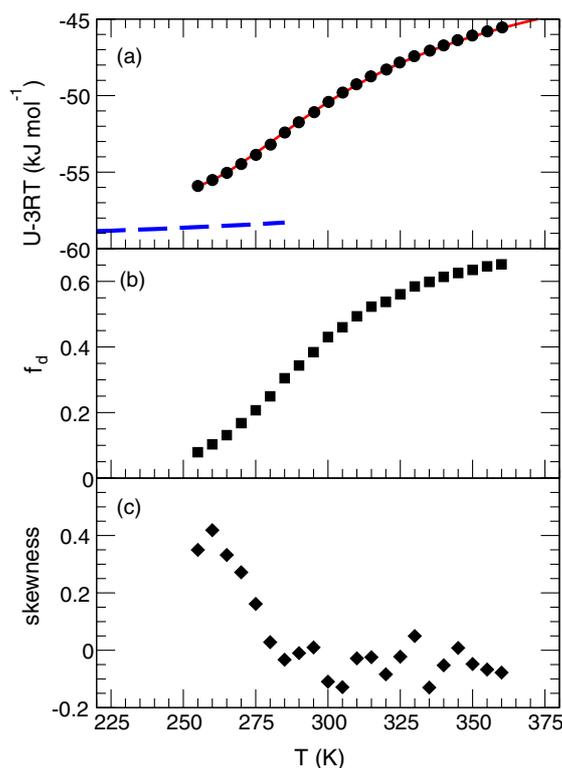
<sup>5</sup> In the case of the  $N = 216$  system, we carry out the same protocol as in the  $N = 1728$  system, 40 times per isochore for the two cases  $\rho = 0.82$  and  $0.83 \text{ g cm}^{-3}$ , each time using a randomized starting configuration to initiate the first run at  $T = 360 \text{ K}$ . Also, the minimum production run time is increased to 500 ps for all state points.



**Figure 2.** Location of the LLC ( $C$ ), spinodals (triangles and diamonds), density extrema ( $\Delta$ ), and response function extrema ( $\Lambda$  and  $\Gamma$ ) in (a) the  $T$ - $P$  and (b) the  $\rho$ - $T$  planes. The symbols used for the various spinodals are the same as in figure 1. Thick lines indicate maxima, and thin lines locate minima.

nearest-neighbour intermolecular bonds are satisfied: the  $T$  dependence of  $U$  approaches an ice-like form, and  $f_d$  approaches zero. The occurrence of inflections in both these curves shows that the region of most rapid change has passed, and that the low  $T$  region in which the density minimum occurs corresponds to the final asymptotic consolidation of the liquid structure towards that of a perfect, defect-free RTN. It is plausible that  $\alpha_P$  should be positive (i.e. normal) for a defect-free RTN; e.g.  $\alpha_P > 0$  for crystalline ice  $I_h$  (an *ordered* tetrahedral network) in this  $T$  range [23]. In this light, the density minimum simply reflects the fact that the process of RTN formation is coming to an end, and so the anomalous  $T$  dependence of thermodynamic properties returns to normal.

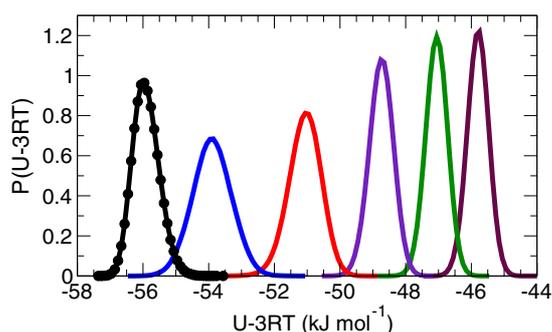
Another indicator that the liquid is approaching the RTN state can be seen in the distribution of values of  $U$ , the potential energy, sampled in our simulations (figure 4). For  $T$  less than



**Figure 3.** Properties of the liquid along the  $\rho = 0.83 \text{ g cm}^{-3}$  isochore as found from the  $N = 216$  simulations. (a) Variation of  $U - 3RT$  with  $T$  for the liquid (circles), compared with  $U - 3RT$  for ice  $I_h$  (dashed line).  $R$  is the gas constant. The solid line through the data points shows  $U - 3RT$  from the fitted EOS.  $U$  for ice  $I_h$  is found from simulations of a proton-disordered configuration of  $N = 432$  ST2 molecules at  $\rho = 0.83 \text{ g cm}^{-3}$ . (b) The fraction of network defects  $f_d$  as a function of  $T$ .  $f_d$  is estimated by evaluating the equilibrium average fraction of molecules not having exactly four nearest neighbour O atoms within 0.35 nm, the distance of the first minimum in the O–O radial distribution function. (c) The skewness of the  $P(U)$  distributions plotted in figure 4. The skewness is evaluated as  $(1/n) \sum_{i=1}^n [(U_i - \bar{U})/\sigma]^3$ , where  $n$  is the number of  $U_i$  values sampled,  $\bar{U}$  is the average value of  $U$ , and  $\sigma$  is the standard deviation of  $P(U)$ .

the inflection in  $U$ , the distribution  $P(U)$  narrows, and also loses its symmetrical shape and becomes skewed, as quantified in figure 3(c). This narrowing and skewing suggests that there is a lower bound on the value of  $U$ , specifically  $U$  for the RTN, and that the system is entering the  $T$  regime where the existence of this lower bound influences the average properties [24].

The location and slope of the  $\Delta_{\min}$  line in figure 1 raises the possibility that a density minimum occurs in ST2 water at positive  $P$  at sufficiently low  $T$ . This, and the generic nature of the mechanism underlying the density minimum found here, demonstrates the potential for the occurrence of density minima in the low  $T$ ,  $P > 0$  behaviour of any tetrahedral liquid having a density maximum. More broadly, our results add to and illuminate the complex behaviour of tetrahedral liquids: the emergence of an RTN structure in these liquids can be understood as the source of their anomalies. Yet the eventual outcome of this RTN-forming process is to bring the liquid closer and closer to a set of near-perfect RTN states that lie at the bottom of the liquid's potential energy landscape [25, 24, 26]. Our simulations show that such a 'liquid at the bottom of the landscape' represents a distinct regime of behaviour:



**Figure 4.** Probability distributions of  $U$  (minus the harmonic vibrational contribution  $3RT$ ) along the  $\rho = 0.83 \text{ g cm}^{-3}$  isochore as found from the  $N = 216$  simulations. From left to right are shown the distributions for  $T = 255, 275, 295, 315, 335$  and  $355 \text{ K}$ .  $R$  is the gas constant.

one that exhibits a number of exotic properties not observed at higher  $T$  (e.g. a crystal-like heat capacity), and also one in which thermodynamic anomalies, so often associated with networking-forming liquids, disappear.

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