Water-like Anomalies from Repulsive Interactions

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In tetravalent network materials like quartz or ice the main interactions are the strong bonds that connect each vertex to four others and the repulsive forces that keep non-bonded vertices further apart. Those interactions, modelled by square wells, are shown to be sufficient to account for the stability of ice-like crystals, with tetrahedral bond angles, at low temperature; endothermic melting of the crystal to a denser water-like amorph at intermediate temperatures; exothermic collapse of the supercooled crystals at high pressure, to a glass, without breaking any bonds; expansion on cooling of both the crystal and the amorph; and a line of spinodal instabilities in the water-like supercooled amorph where the compressibility, heat capacity and negative expansivity diverge.
[water, ice, square well, phase transition, spinodal]

1. Introduction.

Many of the anomalies of ice and water, and related tetravalent network materials like silica, seem to have a common origin: they can be accounted for by repulsions between non-bonded particles at distances greater than a bond length. Some of the anomalies that can be explained by this simple idea are that water is denser than ice, that water, ice and silica expand when cooled¹, that the heat capacity² and compressibility³ of water increase when it is cooled and that supercooled ice⁴⁻⁷ and quartz⁸ collapse exothermically to amorphous solids under pressure.

Repulsions between non-bonded particles provide a natural explanation for expansion on cooling and they also explain the tetrahedral bond angles that are common in tetravalent crystals, because second-neighbours are as far apart as possible when the bond angles are tetrahedral. Pressure applied to the crystal can overcome the repulsions so that the bond angle distribution broadens, allowing the open crystal collapse to a denser amorph⁹, without breaking any bonds. Burdett¹⁰ has noted that repulsions between non-bonded SiO₄ tetrahedra are the main determinant of the bond angles in silicates.

2. The Model.

The tetravalent structural units of water or silica are represented by hard particles of diameter σ , with a square-well of diameter $\lambda\sigma$ that makes the bonds permanent

$$u(r) = \begin{cases} 0 & \text{if } \sigma < r < \lambda\sigma \\ \infty & \text{otherwise} \end{cases} \quad \text{bonded}$$

where r is the separation between the particle centres. The structure and properties of two- and three-dimensional materials, with permanently-bonded honeycomb or diamond network topologies, and with a range of values of λ , were described previously⁹. Results are reported here for the case $\lambda = 1.1$, which allows a 10 % variation in the bond length and allows the bond angles to vary from 60° to 170°.

Non-bonded pairs repel each other, and are prevented from forming bonds, with the potential

$$u(r) = \begin{cases} 0 & \text{if } r > \lambda_h\sigma \\ \epsilon_h & \text{if } \lambda\sigma < r < \lambda_h\sigma \\ \infty & \text{if } r < \lambda\sigma \end{cases} \quad \text{non-bonded}$$

The positive "hump" energy, ϵ_h , provides the repulsions. A similar potential has been used to model soft repulsions^{11,12} and can explain some phase transitions^{11,12}. The diameter of the "hump" is $\lambda_h\sigma$, where $\lambda_h = \sqrt{8/3}$ was chosen so that the four bonded neighbours of a molecule are stable when they are arranged tetrahedrally, as in a diamond lattice. The potential energy of the model is $N\epsilon_h$ where N_h is the number of pairs that are separated by a distance $\lambda\sigma$ to $\lambda_h\sigma$.

3. Simulation details.

$N = 512$ particles were initially placed on a diamond lattice in a cubic cell with periodic boundaries and assigned random velocities. The trajectories were followed in time using the molecular dynamics method^{13,14}. Pairs bounce elastically whenever their separation reaches σ or $\lambda\sigma$ and inelastically, so as to conserve energy, when their separation reaches $\lambda_h\sigma$. The simulations were run with constant volume and energy although the velocities were rescaled about every 2N collisions, where N is the number of particles, to avoid any temperature drift due to round off errors.

The density scale, $z = V_0/V = (N/V)(2\sigma)^3/\sqrt{27}$, is chosen such that $z = 1$ in the perfect diamond crystal when all bonded pairs are at the contact separation σ and all bond angles are tetrahedral. V is the volume of the simulation cell. z can exceed unity because the crystals can deform to denser amorphous structures by varying the bond angles. The density was changed by varying the diameter of the particles linearly with time¹⁴ during the molecular dynamics run. Most runs were started by changing the density or temperature from a previous run at a nearby state point and equilibrating for $2000N(1+2\epsilon_h/kT)$ at the new state point before sampling for the same time. k is the Boltzmann constant and T is the temperature.

Pressures measured for some densities on all isotherms with $N = 216$ and through the phase transition on the $\epsilon_h/kT = 1$ isotherm with $N = 1000$ agree with those shown in figure 1, for $N = 512$, to within the precision. Sciortino *et al*¹⁵ simulated ice in a constant volume cell and in cell of flexible shape at constant pressure. They found that the pressure of the ice, and the pressure where the ice collapsed to an amorph, were almost the same in the two methods.

4. Pressure-volume isotherms.

Figure 1 shows some of the measured pressure-volume isotherms. The model can be stretched to the limiting volume $V/V_0 = \lambda^3 = 1.331$ where all the bonds are at their maximum extension, $\lambda\sigma$, and where the structure is that of a perfect

Figure 1. Pressure versus the volume for some isotherms. Numbers show the inverse temperature ϵ_h/kT . About half the data shown in the unstable region, where $(\partial P/\partial V)_T > 0$, for $1 \leq \epsilon_h/kT \leq 1.8$, were obtained while compressing from the crystal and the others while decompressing from the amorph. The short line labelled 0 shows PV/NkT when $\epsilon_h/kT = 0$. Equilibrium melting of the crystal to the amorph at the pressure of the cusp is exothermic⁷. When $\epsilon_h/kT = 2.6$ the location of the cusp is unreliable because the crystal does not collapse spontaneously. Error bars show the rms variance of values obtained by dividing each run into 20 batches. For the crystals, most error bars are within the line width and do not show. The pressure was also measured along the $\epsilon_h/kT = 0, 0.2, 0.7, 1.2, 2.0, 2.2$ and 2.4 isotherms.

Figure 2. The probability $P(\phi)$, that the angle between two bonds with a common vertex is ϕ , versus ϕ . Results shown are for $\epsilon_h/kT = 2.4$. Squares: the crystal at $V/V_0 = 1.08$ where $PV_0/N\epsilon_h = 14$. Circles: the amorph at $V/V_0 = 0.92$ where $PV_0/N\epsilon_h = 10$. The points are connected by straight lines. $P(\phi)$ was averaged by pooling data in 3° intervals. The peak for the crystal is in the interval $108 - 111^\circ$ that includes the tetrahedral angle, 109.47° .

Figure 3. The radial distribution function $g(r)$ versus r/σ . As for figure 2, with the same two states shown in figure 2, identified by the same symbols. $g(r)$ was measured by pooling data in intervals of $\sigma/20$. The cubic simulation cell has side length 9 to 9.6σ for the density range of the data shown.

Figure 4. A pressure - temperature diagram showing the crystal-amorph equilibrium line, obtained from Maxwell's equal area construction on the isotherms in figure 1. The temperature of maximum density (TMD) is located where adjacent isotherms cross in figure 1. The spinodal line is the locus of the minima on the isotherms for the supercooled amorph from figure 1.

diamond crystal. When $V/V_0 > 1.25$, the pressure follows the empirically determined⁹ limiting form $PV/RT = 2.56/(1 - \lambda^3 V_0/V)$. As the volume is decreased from that limit, four distinct behaviours are observed, depending on temperature.

At high temperatures, $\epsilon_h/kT < 0.9$, the stretched crystal transforms, without any evident discontinuity in the pressure-volume isotherms, to a high density amorph, as shown by the line for $\epsilon_h/kT = 0.5$ in figure 1.

At low temperatures, $\epsilon_h/kT \geq 2$, the pressure varies in a continuous manner from the low-density diamond crystal with $V/V_0 = \lambda^3$ to a metastable high-density diamond crystal, with $V/V_0 = 1$, and it diverges as $PV/NkT = 3/(1 - V_0/V)$ as $V_0/V \rightarrow 1$. These low-temperature high-density crystals are metastable relative to a denser amorph when $PV_0/N\epsilon_h > 16$. The more stable amorph can be formed by cooling a warmer amorph, but it does not nucleate from the crystal on the simulation time scale of 10–15 million collisions when $\epsilon_h/kT \geq 2$.

When $\epsilon_h/kT = 0.9$ and 1.0 the crystal “melts” and the pressure is constant over a finite density range where two phases appear to coexist. There is an upper critical temperature for the “melting” transition, close to $\epsilon_h/kT = 0.9$, where the volume and enthalpy differences between the two phases are zero to within their uncertainties. In common with real water and ice, the amorph is denser than the crystal. There is no indication of a critical point on the melting line for real ice: the volume difference between stretched water and ice¹⁶ extrapolates to zero near -150 MPa but the (extrapolated¹⁶) enthalpy difference remains substantial there.

When $1.2 \leq \epsilon_h/kT \leq 1.8$ the crystal supercools and the pressure-volume isotherms develop a cusp (figure 1). At the cusp the amorph nucleates from the crystal and the pressure decreases as the volume is decreased further. The region where $(\partial P/\partial V)_T > 0$ is thermodynamically unstable and in a constant pressure simulation the crystal would probably collapse to the more stable amorph at the pressure of the cusp. In the present simulations, the imposed constant volume conditions prevent that collapse and the unstable region can be traversed in either direction with minimal hysteresis. When $\epsilon_h/kT = 1.8$, nucleation of the amorph occurs only in the small density range $0.91 \leq z \leq 0.92$, where it always occurred within a few million collisions, but the crystal was simulated for 15 million collisions at $z = 0.89$ and $z = 0.93$ without collapsing. Nucleation of the amorph is evidently a coordinated process that requires the simultaneous distortion of several bond angles, with a large energy barrier that makes it sensitive to temperature coupled to geometrical barriers that make it sensitive to density.

From a thermodynamic viewpoint, the spontaneous transformation of the metastable crystal to a state that is unstable (ie. $(\partial P/\partial V)_T > 0$) is provocative. It cannot be attributed to a spinodal instability in the crystal because the crystal exists both above and below the pressure where the collapse occurs (when $\epsilon_h/kT \geq 1.5$), and because there is no sign of a compressibility increase in the crystal as it approaches the cusp. In that respect the present results differ from another simulation study of crystal collapse¹⁵, and from the predictions of the perturbation theory⁹.

Figure 2 shows that the bond angle distribution in the crystal peaks sharply in the $108-111^\circ$ interval that includes the tetrahedral angle (109.47°) while it is broad in the amorph. Figure 3 shows that radial correlations span the simulation cell for the crystal, but $g(r)$ is close to unity beyond three diameters for the amorph.

The pressure-volume isotherms provide the crystal-amorph equilibrium pressure, the locus of the cusp, the locus of the temperature of maximum density (TMD) in the amorph, and the spinodal line, which corresponds to the minima on the isotherms for the amorph. Those lines are shown in the pressure-temperature diagram, figure 4. The anomalous properties of supercooled water are explained by the spinodal line in figure 4 because the compressibility, heat capacity and (negative) expansivity of the supercooled amorph diverge as it is cooled along an isobar towards the spinodal line.

The results raise some awkward questions. Phases with different geometrical symmetry should be separated by a line of phase transitions, which cannot end at a critical point because the two phases cannot become identical. However, at high temperature the open crystal at $V/V_0 = \lambda^3$ compresses to an amorph with no evident discontinuity in the pressure, and at low temperatures there is a line of first-order crystal-amorph transitions that ends at a critical point. There is possibly a change in the slopes $(\partial P/\partial V)_T$ when $V/V_0 \approx 1.143$ and $\epsilon_h/kT < 0.9$, consistent with the line of first order transitions becoming an isochoric line of second order transitions above the critical temperature.

5. Thermal effects.

Heat is absorbed when ice melts to water but heat is released when supercooled ice collapses under pressure to an amorphous solid⁷. The exothermic effect is a general characteristic¹⁷ of the collapse of crystals to amorphous solids and distinguishes it from equilibrium melting¹⁷.

Figure 5. The pressure $PV_0/N\epsilon_h$ and the enthalpy H/NkT versus volume V/V_0 on the $\epsilon_h/kT = 1.5$ isotherm. Maxwell's equal area construction locates the tie-line at $PV_0/N\epsilon_h = 8.5$ and it locates the volumes of the two phases at equilibrium. The negatively-sloped solid line connects the enthalpy of the amorph to that of the crystal at their equilibrium volumes and shows that melting is endothermic. The dashed horizontal line connects the crystal at the cusp to the amorph at the same pressure. The positively sloped dashed line connects the enthalpies of the crystal, at the cusp, to that of the amorph at the same pressure, and shows that the isobaric collapse of the supercooled crystal is exothermic.

Figure 5 shows the pressure and enthalpy of the crystal and amorph on the $\epsilon_h/kT = 1.5$ isotherm. The enthalpy is $H = U + PV$ where the energy $U = N_h \epsilon_h + (3/2)NkT$. The equilibrium melting pressure is located by Maxwell's equal area construction. Figure 5 shows that the crystal has the lower enthalpy at the equilibrium melting pressure, so that equilibrium melting is endothermic. The heat released when the amorph freezes at the equilibrium pressure is 1.5 ± 0.5 NkT, which is intermediate between the heat released when the low density form of glassy water freezes (irreversibly) to cubic ice near 150 K (1.05 NkT¹⁸) and the heat released when liquid water freezes at 273 K (2.6 NkT).

Figure 5 shows that heat is released when the supercooled crystal collapses from the cusp to the amorph at the same pressure. The heat released is 1 ± 0.5 NkT. The collapse is exothermic because it is driven by the large negative $P\Delta V$ contribution to the enthalpy change, which overcomes the increase in energy.

The uncertainties in the estimated enthalpy changes are large but the same trends are shown on all isotherms $1.8 \geq \epsilon_h/kT > 1$. When $\epsilon_h/kT > 1.8$ the crystal does not collapse spontaneously and the location of the cusp is uncertain. The enthalpy of melting is 0.5 ± 0.3 NkT when $\epsilon_h/kT = 1$ and 0 ± 0.3 NkT when $\epsilon_h/kT = 0.9$.

6. Density maximum.

The density maximum, where $\alpha = 0$, is located where two adjacent isotherms cross in figure 1. The locus of the density maximum in the amorph (figure 4) differs from that in real water, where the pressure at the density maximum decreases with temperature. This is because the permanent bonds limit the expansion of the model at high temperature.

The pressure-volume isotherms for the crystal also cross (figure 1) when $\epsilon_h/kT \geq 1.5$ and $V/V_0 = 1.16$, so the model crystal also expands when cooled. Real ice expands when cooled¹ below 63 K at atmospheric pressure.

Where the density maximum, $\alpha = 0$, meets the spinodal line, where α diverges, (figure 4) α must change from $-\infty$ to $+\infty$ and thermodynamics requires^{19,20} that the slope of the spinodal line, $(dP/dT) \sim \alpha/\kappa$, where κ is the compressibility, must also change sign. Debenedetti and De Antonio²¹ provide a detailed analysis of the thermodynamic properties near that intersection. The uncertainty in $P_s(T)$ is about 5% when $kT/\epsilon_h \leq 1/2$, but there is no doubt that it goes through a maximum (figure 4) when $kT/\epsilon_h \approx 1/2$, because its slope is required to change sign when it intercepts the locus of the density maxima. If the slope changed sign the other way, with a $T_s(P)$ minimum rather than a $P_s(T)$ maximum, then the spinodal line would cross the melting line into the region where the amorph is the stable phase, which is not possible.

The maximum in the spinodal pressure (figure 4) is intriguing. On an isobar just below the maximum the amorph cannot exist as a metastable phase between the two temperatures where the spinodal line crosses the isobar, but it can exist both at higher and at lower temperatures on the same isobar. In other words, there is a stability gap in amorphous phase space. There is also a stability gap in real water between 160 K and 232 K at atmospheric pressure: liquid water always freezes²² above 232 K, except for small drops^{23,24} cooled at rates approaching -10^6 K/s, and glassy water always freezes^{4,7,18,23} when warmed above 160 K. With the exception of very small drops²⁴ and thin films²⁵, amorphous water has not been observed in that stability gap.

7. Structure at the spinodal.

A spinodal^{3,19,20,21} has structural implications because a divergence of the compressibility implies divergences in density fluctuations and in the density-density correlation length²⁶. Those divergences arise from some structural correlations, which are the ultimate cause of the spinodal, and because the model is so simple the identification of the correlated structures is straightforward.

The significant local structural variable in the model is the bond angle and the simplest correlation to look for is a clustering of tetrahedral bond angles, associated with local fluctuations in the volume and enthalpy, towards their values in the diamond crystal.

A simple way to locate clusters of tetrahedral bond angles is to identify crystal-like (c) particles as those which have no repulsive interactions, ie those whose twelve second neighbours are all more than $\lambda_h \sigma$ distant. Each crystal-like particle is at one end of twelve bond angles, all of which must be near to or greater than the tetrahedral angle. Crystal-like particles reside in a low density environment, because they have only four other particles within the distance $\lambda_h \sigma$, and they have zero potential energy. Figure 6 shows the radial distribution function, $g_{cc}(r)$, for those particles and compares it to $g(r)$ for all the particles. On average, there are only nine crystal-like particles in each configuration of $N = 512$ particles, near the spinodal when $\epsilon_h/kT = 1.5$. Figure 6 shows that correlations between crystal-like particles are sharp and they extend across the simulation cell, so there are long range correlations between clusters of near-tetrahedral bond angles at the spinodal.

Figure 6. The radial distribution functions $g(r)$ and $g_{cc}(r)$ versus r/σ near the spinodal when $N = 512$, $\epsilon_h/kT = 1.5$ and $V/V_0 = 1.06$ (figure 5). circles : $g(r)$ for all the particles; squares: $g_{cc}(r)$ for crystal-like particles that make no repulsive interactions and are therefore at the ends of twelve bond angles that are near to or greater than the tetrahedral angle. Results beyond 2.2 diameters are amplified by 10. The average number of crystal-like particles is 9.

8. Conclusions.

The simple model, that uses only spherically symmetrical square well forces, behaves like real water and ice: The ice-like crystal melts endothermically to a denser water-like amorph. The supercooled amorph expands when it is cooled and it has a spinodal line where the compressibility, heat capacity and (negative) expansivity diverge. The ice-like crystal also expands when cooled at low temperature. The supercooled ice collapses exothermically to a high density amorph at high pressure. Thus, the model captures a variety of previously unrelated anomalies and shows that all that is required to explain them are strong bonds and repulsions between non-bonded particles. An unexplained feature of the model is that the crystal-amorph melting line ends at a critical point (figure 4).

The phase diagram for the model (figure 4) is an inversion of the familiar van der Waals' diagram for the gas-liquid transition, in the sense that the coexistence line ends at a lower critical pressure, rather than an upper critical pressure. A van der Waals gas condenses to a denser liquid because the molecules attract. In the present model it is the broad distribution of bond angles in the amorph that condenses to a narrow distribution in the less dense crystal, due to the repulsions. The second critical point scenario proposed by Poole *et al*²⁷, which is supported by the recent work of Tanaka²⁸ and Harrington *et al*²⁹, calls for a phase transition with a lower critical pressure. The model shows how this phenomenology can arise naturally from repulsions between non-bonded particles in a network. It seems likely that this behaviour can also occur in a model that allows the bonds to break and form a topologically disordered network.

Figure 7. The pressure versus temperature for a fluid model that allows the bonds to break, at density $z = 0.9$. A saturated square well model SSW($Nv = 4$, $\lambda = 1.1$, no Δ , $\epsilon = \epsilon_b$), is supplemented by the same repulsive hump between non-bonded particles that was used in the permanently bonded case. The fluid was equilibrated and run for $100N\exp(2\epsilon/kT)$ collisions, corresponding to about 12 bond lifetimes, at each temperature shown. Despite the long runs, the precision is poor, but the results show that the fluid would expand by about 6% when cooled from $kT/\epsilon = 0.28$ to 0.24 at constant pressure. At the lowest temperature shown the fluid becomes glassy.

Exploratory studies of a model tetravalent fluid which has the same λ and λ_b , but allows bonds to break and reform in different network topologies, show that the liquid expands when cooled, (figure 7) but the simulations must be orders of magnitude longer for the precision of the pressure measurements to approach that of the permanently bonded model in the vicinity of the density maximum. The model fluid also shows hysteresis loops when cooled and warmed along some isochors, which is consistent with an underlying phase transition of the kind proposed by Poole *et al*²⁷, but further work is needed to show that a model of this kind can display two liquid phases.

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