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Is there a re-entrant spinodal in liquid water ?

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The supercooled and stretched regions of the phase diagram of simulated liquid water are investigated by calculating the equation of state of the ST2 pair-potential. We find that simulated water does not display a re-entrant spinodal and that the projection of the density maximum line in the plane of pressure and temperature becomes positively sloped on stretching. The well known anomalous behavior of supercooled water is tentatively associated with the existence of an inaccessible critical point. Evidence is presented that suggests the association of this new critical point with the transition between low density and high density amorphous solid water.

Nous avons étudié la région super-refroidie et étirée du diagramme de phase de la simulation de l'eau liquide en calculant l'équation d'état. Nous avons trouvé que la simulation de l'eau ne montre pas de "reentrant-spinodal" et que la ligne de densité maximum étirée se penche avec dérivée positive sur le plan pression-température. Nous avons tenté d'associer le comportement anormal bien connu de l'eau super-refroidie à l'existence d'un point critique inaccessible. Nous présentons des évidences qui suggèrent l'association de ce nouveau point critique à la transition entre basse et haute densité de l'eau solide amorphe.

Liquid water is one of the most studied complex liquids. The possibility for the water molecule to form hydrogen bonds and to create an open network in both the solid and the liquid phases is at the basis of its peculiar behavior. The inverse correlation between the energy and the volume at a microscopic level, due to the strength and directionality of the hydrogen bond, is reflected in the anomalous behavior of the liquid state. In the supercooled and the stretched regions of the phase diagram, the well-known anomalies of liquid water become more pronounced [1,2]. The effects of the hydrogen bond network become more and more important with decreasing temperature (lowering of the local energy) as well as with increasing

negative pressure (increasing of the local volume) [3]. In this article we give a preliminary report of a study on the phase behavior of metastable water based on analyses of extensive molecular dynamics simulations with a water-water potential that mimics the anomalous behavior of the real liquid.

The well-known equilibrium phase diagram of water is shown in Fig. 1. When the equilibrium solid-liquid or liquid-gas lines are crossed, the liquid enters into a thermodynamic state that is metastable compared to the solid or to the gas. The liquid can be supercooled or stretched only to a finite extent. Then, even in very clean samples, internal fluctuations drive the system from the metastable liquid state to the stable solid or gas phase, imposing a limit on the range of thermodynamic states accessible to experiments. These limits of supercooling and stretching define the lines of homogeneous nucleation.

Fig. 1: Phase Diagram of water: Solid lines indicate the liquid-gas and the liquid-solid equilibrium boundaries. Full circles indicate the limit of homogeneous nucleation. The dashed line is the spinodal line associated with the liquid-gas critical point.

Another important thermodynamic line is given by the limit of stability of the liquid. As this line is crossed, the system becomes unstable and any fluctuation, no matter how small, is able to drive the system into a new phase. In mean field approximation, the system is stable whenever

$$\left(\frac{\partial^2 A(V, T)}{\partial V^2} \right)_T = - \left(\frac{\partial P}{\partial V} \right)_T > 0$$

where $A(V, T)$ is the Helmholtz potential, V is the specific volume, P the pressure and T the temperature. In Fig. 2 we show the P versus V isotherms for the mean field (van der Waals) case. We see that the point

marked o separates the stable liquid phase from the unstable phase, while the point x marks the equilibrium point between the gas and the liquid phases. The liquid is metastable between x and o . Fig. 2 also makes clear that the van der Waals theory predicts the possibility of metastable liquid states at negative pressure. The line connecting the o points as a function of T and P gives information on the limit of stability of the liquid. This line, named the spinodal line, is also shown in Fig. 1. On approaching the spinodal line, one observes an increase in the isothermal compressibility K_T and in the isobaric specific heat C_P . Indeed, as shown by Compagner [4], these quantities diverge following a power-law form at the spinodal line, with exponents of -1 .

Fig. 2: Van der Waals isotherms around the critical point ($T_c = 1, V_c = 1, P_c = 1$). The $T=1.2$, $T=1.0$, $T=0.8$ and $T=0.6$ isotherms are shown.

While the gas and the liquid phases have the same symmetry, the liquid and the solid phases cannot be described by the same free energy surface and no liquid-solid second order critical point exists. However, this fact does not prevent the possibility that the liquid or the solid free energy hypersurfaces terminate in the metastable region in a spinodal line. Indeed, recent work on stretched and compressed tetrahedral crystals seems to suggest that the metastable region in solids might terminate in a spinodal instability under particular conditions [5]. In the case of liquids, this line of reasoning was pursued 16 years ago by Speedy and Angell [6]. Triggered by the observation that liquid water shows an anomalous increase in C_P and K_T on cooling, they postulated the existence of a thermodynamic anomaly in the free energy of the supercooled liquid. They argued that this anomalous line should run parallel to the homogeneous nucleation line on the experimentally inaccessible side. Since then, many static and dynamic quantities

have been studied and shown to satisfy a power law relation at the lowest temperatures, as expected for such quantities near a spinodal [7–12]. However, theories which are not based on the existence of critical behavior in the supercooled region are also able to reproduce the experimental data with functional forms other than a power law [13].

Further important progress in this field has been made by Speedy [8] for the case of water and generalized to arbitrary fluids by Debenedetti and his colleagues [14–18]. They have observed that liquids having a line of density maxima which has a negative slope in the P - T plane of their phase diagram should possess a region where the line of density maxima and the liquid spinodal line meet. Based on thermodynamic argumentation, they show that the spinodal must change slope at the point where it meets the line of density maxima. This phenomena means that the usual liquid spinodal can turn upward and be “re-entrant” from negative pressure back to positive pressure in the supercooled region of the phase diagram. This conclusion supports the possibility that the anomalies observed at positive pressure and low temperature are indeed connected with the ones observed at negative pressures. If this is the case, such a re-entrant spinodal represents a continuous limit of stability bounding the entire liquid state, preventing any continuity between amorphous ice and liquid water.

To test these hypotheses and to shed light on the behavior of liquid water in the metastable region, we perform an extensive set of simulations in the stable and metastable regions of the liquid state. Computer simulations are particularly suitable for this kind of study because of the absence of any boundary and of any impurity, which in real experiments prompt heterogeneous nucleation. The limitations are given by the finite size of the simulation box and by the available computer time. At low temperatures and close to a pseudo-critical point, slowing down of the dynamics is expected. Hence we have chosen to work with a small set of particles but to perform very long equilibration and production runs.

We perform simulations consisting of systems of 216 particles enclosed in a cubic box with periodic boundary conditions. The effect of long range Coulomb forces is estimated with the reaction field method. The number of particles and size of the simulation box are fixed to give the desired specific volume, and initial equilibration to a desired temperature is achieved using Berendsen’s velocity rescaling method, using a decay constant of 0.5 ps [19]. The time step for the update of particle positions is fixed at 1.0 fs. Equilibration was considered complete when the unconstrained thermodynamic properties (pressure and potential energy) had relaxed into a steady state. We also check that particles had diffused a rms distance of at least one molecular diameter from their starting positions to avoid trapping in glassy states. Also, in almost all cases, a given simulation was started using the final particle positions of a previous simulation at as

near a state point to the new one as was possible. The lengths of the runs (equilibration plus production) varied depending on the time needed to obtain reliable equilibration and measurements, but in no case were less than 250 ps. Due to the slow relaxation seen in the systems at the lowest temperatures and highest specific volumes, run times of 600 to 1000 ps were common. By calculating the pressure for each of the temperatures and volumes studied, we have reconstructed the $P(V,T)$ surface in a large part of the supercooled and stretched regions of the phase diagram.

Fig. 3: Isochores at density 1.0 gm/cm^3 from experimental data (full line), TIP4P potential ($\square$), SPC/E potential ($\triangle$), and ST2 potential ($\circ$).

Because the density maximum phenomenon is tightly connected with the possibility of a re-entrant spinodal, simulations with the chosen water-water potential must exhibit, as a function of temperature, a density maximum at constant pressure or a pressure minimum at constant volume. For this reason, we first perform simulations at a fixed density (1.0 gm/cm^3) as a function of temperature for different potentials commonly used to model liquid water. The resulting P - T isochores are shown in Fig. 3, together with the experimental data [20]. All the potentials show a density minimum, even if at different temperatures and pressures. Compared with the experimental density maximum, the SPC/E and TIP4P density maxima are shifted toward lower temperatures while the ST2 density maximum is found at higher temperatures, in agreement with the early measurements of Stillinger and Rahman [21].

This apparent drawback of the ST2 potential is very useful for our numerical study. Indeed the higher temperature of the ST2 density maximum allows equilibrium simulations of states up to 100K below its

TMD. Therefore, ST2 can be used to probe the thermodynamic properties and structure of the system in the region both where the liquid is strongly anomalous, and where the re-entrant spinodal is predicted to be found. For this reason, we choose to study assemblies of ST2 particles.

Fig. 4: ST2 P - V isotherms at $T = 390\text{K}$ (∇), $T = 360\text{K}$ ($\triangle$), $T = 330\text{K}$ ($\square$) and $T = 290\text{K}$ ($\circ$). This figure shows the P - V isotherms at four temperatures. At all the temperatures we are able to simulate metastable states at negative pressure. The 390K, 360K and 330K P - V isotherms show van der Waals like behavior on stretching. The volumes and the pressures at which the system become unstable are a decreasing function of the temperature as expected in the case of normal liquids. The 290K P - V isotherm crosses the 330K P - V isotherm, displaying the existence of a density maximum at this temperature (i.e. a density maximum is a pressure minimum at constant volume). Interestingly enough, the spinodal pressure P_s at this temperature is *lower* than P_s at $T = 330\text{K}$, indicating that the spinodal line $P_s(T)$ does not turn around but continues decreasing in pressure on lowering the temperature.

As we have noted above, the density maximum line if **negatively sloped in the P - T plane** must meet the spinodal line, forcing it to become re-entrant. Because ST2 water has a negatively-sloped density maximum line at positive pressures and a monotonically decreasing spinodal, we predict that the density maximum line in ST2 water must change slope in the vicinity of the liquid spinodal. To test this prediction, we calculate the P - T isochores for different densities and find for each density the temperature at which the pressure is at a minimum (Fig. 5). The line of density maxima thus calculated is found to change slope around density 0.9gm/cm^3 , avoiding the intersection with the spinodal line (shown as a full line), and the

Fig. 5: ST2 isochores for different densities. From top to bottom: 1.10gm/cm^3 , 1.05gm/cm^3 , 1.0gm/cm^3 , 0.95gm/cm^3 , 0.9gm/cm^3 , 0.85gm/cm^3 , 0.8gm/cm^3 . The full line connecting the filled circles is the spinodal line for the ST2 potential.

thermodynamic behavior predicted by Speedy and Debenedetti. We are led to conclude, on the basis of the data shown in Fig. 5 that the liquid spinodal is **not re-entrant** in ST2 water. This conclusion has been independently reached for ST2 by Strieman [22].

But, if the spinodal is not re-entrant, what is the origin of the increase in C_P and K_T in the supercooled region? Is the ST2 potential able to reproduce this anomalous behavior with a mechanism different from that occurring when there is a re-entrant spinodal? To address these questions, we have calculated the P - V isotherms at lower temperatures. As shown in Fig. 6, on lowering the temperature the isotherms develop a stronger and stronger inflection which ends in a critical isotherm around 220K. The data shown in Fig. 6 are indeed very similar to the van der Waals isotherm shown in Fig. 2 once we remember that, being in the region with negative expansion coefficient, the pressure increases at constant volume on decreasing the temperature. ST2 water thus seems to display a novel critical point c' at about $T_{c'} = 220\text{K}$ and $P_{c'} = 200\text{MPa}$ at a density close to 1.0gm/cm^3 .

If this critical point exists then we should be able to identify two phases with the same symmetry and a coexistence line between them. To investigate the structural difference between the two phases we study the structure of the liquid at a temperature close to but lower than $T_{c'}$ at two densities far from the critical density. This is the same as looking at the structure of a liquid-gas system along a supercritical isotherm for densities respectively smaller and larger than the liquid-gas critical density. In this case the

Fig. 6: ST2 P - V isotherms at $T = 235\text{K}$ ($\square$), $T = 250\text{K}$ ($\triangle$), $T=273\text{K}$ ($\triangle$) and $T=290\text{K}$ ($\diamond$).

high density structure would resemble the liquid structure, while the low density structure would resemble the one characteristic of the gas phase. The comparison between the two ST2 structures is shown in Fig. 7, where we show the $h(r)$ function, i.e., the neutron-averaged Fourier transform of the structure factor, for density 0.92gm/cm^3 and 1.05gm/cm^3 at $T = 235\text{K}$. The difference between the two structures strikingly resembles the difference observed experimentally between the structures of high density amorphous (HDA) and low density amorphous (LDA) ice [23,24].

Then, in ST2 water, for pressure lower than 200 MPa, it is possible to find completely reversible paths continuously connecting states where the structure of the liquid is similar to the HDA and to the LDA structure. In the same range of pressure, a completely reversible path connects the low temperature glassy state to the normal liquid.

As is well known from the theory of critical phenomena [25], the presence of a critical point affects the response functions in an area around the critical point; as seen in Fig. 6, the supercritical isotherms are affected by the existence of the critical point. Along paths in the P - T plane in the one-phase region (i.e. on lowering the temperature at constant pressure) one expects maxima in C_P and in K_T because the response functions increase on approaching the critical point and decrease on getting further away.

Are the experimentally-observed increases in C_P and K_T related to the existence of an unreachable critical point ? To test this possibility we compare C_P and K_T calculated from our simulations with the experimentally measured C_P and K_T . We compare the experimental data for each temperature and pressure

Fig. 7: Neutron-averaged Fourier transform of the structure factor $h(r)$. Dashed line: $\rho = 0.92\text{gm/cm}^3$; full line: $\rho = 1.05\text{gm/cm}^3$. In the inset, the experimentally measured $h(r)$ functions for the low density amorphous ice (dashed line) and the high density amorphous ice (full line) from Ref. 24 are shown.

with the corresponding ST2 data at temperature 34 degrees higher and a pressure 95 MPa higher to take into account the different position of the density maxima in the P - T plane. To support the validity of this procedure, we show in Fig. 8 the comparison of the experimental density at atmospheric pressure with the shifted ST2 data. The agreement is rather good. Using the same shift we compare in the two following figures C_P and K_T . Again remarkable agreement is observed, both qualitatively and quantitatively.

The agreement between the experimental data and the ST2 shifted data appears to validate the description of the liquid state offered by our ST2 calculations. However, the results shown here must be submitted to extensive tests, using different potentials and much larger systems. The importance of this task argues for a strong effort in implementing MD programs for water-like potentials on new powerful parallel computers. Analytical work on simple potentials showing a density maximum should also be performed.

If our data are confirmed by these extensive checks, then it will become important to perform experiments as close as possible to the new critical point, which according to the P and T shift used above, should be located in real water at $T = 185\text{ K}$ and $P = 120\text{ MPa}$. At the same time, we hope that measurements in the stretched region can be extended to search for the change in slope of the line of density maxima [26].

In summary, the ST2 data show no re-entrant spinodal at negative pressure. They do show a novel critical point at low temperature and high pressure, which appears to be related to a transition between two

Fig. 8: Temperature dependence of the density at atmospheric pressure in water ($\square$) and simulated ST2 water ($\circ$).

Fig. 9: (a) Temperature dependence of K_T at atmospheric pressure in water ($\square$) and simulated ST2 water ($\circ$). (b) Temperature dependence of C_P at atmospheric pressure in water ($\square$) and simulated ST2 water ($\circ$).

structures that we have shown to be similar to the HDA and LDA structures. Also ST2 data do not predict any "real" critical behavior in K_T or C_P , but rather a maximum in K_T and C_P for pressures lower than the

critical pressure. The high density structure (defective tetrahedral network) that smoothly transforms into the low density structure (random tetrahedral network) on lowering the temperature is reminiscent of the progressive growth of four-bonded clusters implied by the Stanley and Teixeira model [13]. The temperature at which K_T is maximum, which indicates the point of smooth transition between the two structures in the ST2 system, is similar to the percolation point of low density tetrahedrally coordinated molecules in the Stanley-Teixeira model.

The ST2 data also support the possibility of a continuity of states connecting liquid water with the amorphous substance obtained experimentally by hyperquenching small liquid droplets or by vapor deposition. On a slow cooling of the liquid, the glass transition is prevented by the homogeneous nucleation event. Indeed, since the growing cluster has a structure with a local order roughly similar to the ice structure, the probability that one of these clusters will have the correct shape (topology) and size to irreversibly transform the system into the solid state is large. The ST2 data also suggest that the amorphous substance that one obtains at low temperature and atmospheric pressure is, if truly in metastable equilibrium, on the same free energy surface as the liquid state. From an experimental point of view the situation is still unclear. The possibility of a continuity of states between amorphous and liquid phases [27,28] as well as the opposite behavior [29] has been suggested on the basis of different thermodynamic arguments based on measured values of C_P and estimated entropies. Molecular dynamics simulations, where the nucleation event can be bypassed by the cleanness of the sample and by the finite size, should be used to refute or confirm these arguments.

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- [1] Angell, C. A. *Ann. Rev. Phys. Chem.* **34**, 593–630 (1983).
- [2] Angell, C. A. in *Water: A Comprehensive Treatise*, Ed. F. Franks (Plenum, New York, 1982), Ch. 1.
- [3] Stanley, H. E., Teixeira, J., Geiger, A. & Blumberg, R. L. *Physica* **106A** 260–277 (1981).
- [4] Compagner, A. *Physica* **72** 115 (1974).
- [5] Sciortino, F., Stanley H.E., Shao J., Wolf G. and Angell, C.A, submitted to *Phys. Rev. Lett.*
- [6] Speedy, R. J. & Angell, C. A. *J. Chem. Phys.* **65**, 851–858 (1976).

- [7] Oguni, M. & Angell, C. A. *J. Chem. Phys.* **78**, 7334–7342 (1983).
- [8] Speedy, R. J. *J. Phys. Chem.* **86**, 982–991 (1982).
- [9] Speedy, R. J. *J. Phys. Chem.* **91**, 3354–3358 (1987).
- [10] Hare, D. E. & Sorensen C. M. *87*, 4840–4845 (1987).
- [11] Prielmeier, F. X., Lang, E. W., Speedy, R. J. & Lüdemann, H.-D. *Phys. Rev. Lett.* **59** 1128–1131 (1987).
- [12] Prielmeier, F. X., Lang, E. W., Speedy, R. J. & Lüdemann, H.-D. *Ber. Bunsenges. Phys. Chem.* **92** 1111–1117 (1988).
- [13] Stanley, H. E. & Teixeira, J. *J. Chem. Phys.* **73** 3404–3422 (1980).
- [14] Debenedetti, P. G. & D'Antonio, M. C. *J. Chem. Phys* **84** 3339–3345 (1986).
- [15] Debenedetti, P. G. & D'Antonio, M. C. *J. Chem. Phys* **85** 4005–4010 (1986).
- [16] D'Antonio, M. C. & Debenedetti, P. G. *J. Chem. Phys* **86** 2229–2235 (1987).
- [17] Debenedetti, P. G. & D'Antonio, M. C. *AIChE J.* **34** 447–455 (1988).
- [18] Debenedetti, P.G., Raghaven, V.S. & Borick, S.S. *J. Phys. Chem.* **95** 4540–4551 (1991).
- [19] Berendsen, H. J. C., Postma, J. P. M., van Gunsteren, W. F., DiNola, A. & Haak, J. R. *J. chem. Phys.* **81** 3684–3690 (1984).
- [20] Haar, L., Gallagher, J. S. & Kell, G. S. in *National Bureau of Standards – National Research Council Steam Tables* (McGraw-Hill, New York, 1985).
- [21] Stillinger, F.H. and Rahman, A. *J. Chem. Phys.* **60** 1545–1557 (1974).
- [22] Strieman, L. *Ph.D. Thesis University of Dortmund* (Dortmund 1992).
- [23] Chowdhury, M. R., Dore, J. C. & Wenzel, J. T. *J. Non-Cryst. Solids* **53** 247–265 (1982).
- [24] Bellisent-Funel, M.-C., Teixeira, J. & Bosio, L. *J. chem. Phys.* **87**, 2231–2235 (1987).
- [25] Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971).
- [26] Green, J. L., Durben, D. J., Wolf, G. H. & Angell, C. A. *Science* **249** 649–652 (1990).
- [27] Hallbrucker, A., Mayer, E. & Johari, G. P. *Phil. Mag.* **60**, 179–187 (1989).
- [28] Whalley, E., Klug, D. D. & Handa, Y. P. *Nature* **342** 782–783 (1989).
- [29] Speedy, R. J. *J. Phys. Chem.* **96**, 2322–2325 (1992).