

Proposed high-pressure calorimetric experiment to probe theoretical predictions on the liquid-liquid critical point hypothesis

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A high-pressure calorimetric experiment to test the validity of a water model's prediction, regarding the behavior of the heat capacity in the liquid-liquid critical point and singularity-free scenarios, is proposed in this paper. The response of the specific heat at high pressure is different depending on the existence, or not, of a second critical point. If the model presents a second critical point, there is a nondivergent maximum in the specific heat at a temperature $T \sim T_c$ for any pressure $P > P_c$ (T_c and P_c being the temperature and pressure of the model's second critical point). This maximum does not appear for the model with a singularity free scenario.

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I. INTRODUCTION

Liquid water exists in a metastable supercooled state far below the melting temperature. A number of thermodynamic response functions of supercooled water, such as the isothermal compressibility and the constant pressure specific heat, show a sudden increase when cooling down to $T \sim 228$ K and $P = 1$ atm [1,2]. In order to explain these anomalies several theories have been proposed.

The liquid-liquid phase transition hypothesis [3] proposes the existence of a first order line of phase transitions separating two liquid states of different densities: the high density liquid (HDL) and the low density liquid (LDL) state. This line of phase transitions has a negative slope in the P - T phase diagram and ends up in a critical point at $T_c \sim 200$ K and $P_c \sim 1.7$ kbar. The increase on the thermodynamic functions as a power law divergence holds only at the critical point. For smaller pressures the increase is just a fluctuation induced by the Widom line. Another possible scenario is singularity free [4,5]. In this scenario the anomalies found in the experiments are not considered to end up in real singularities but in nondivergent maxima due to the anticorrelated fluctuations of volume and entropy.

The direct observation of a possible first order liquid-liquid phase transition line and a second critical point in water has been hampered by the appearance of the homogeneous nucleation process which takes place at higher temperatures [$T_H(P)$], than the ones corresponding to the hypothesized coexistence line. In this paper we focus our attention on the following question: Can we expect any difference [at temperatures $T > T_H(P)$] in the calorimetric response of supercooled water depending on the existence, or not, of a second critical point?

II. THE MODEL

In order to give a possible answer to this question we consider a liquid model, previously proposed for the singularity free scenario [4], where the existence or not of a sec-

ond liquid-liquid critical point is easily tunable. The model is described in detail in Ref. [6]. In the liquid phase, each water molecule interacts with four other water molecules forming hydrogen bonds with energy $-J$. The formation of a hydrogen bond increases the volume of the system by a certain amount δV . In the simplest version of this model, there is no correlation between the possible four hydrogen bonds formed by a particular water molecule. The correlation length related to the formation of the hydrogen bond network does not diverge and the thermodynamic response functions present a simple (nondivergent) maximum at a temperature $T_h(P)$. This temperature $T_h(P)$ is always proportional to the absolute value of the interaction energy due to the formation of a hydrogen bond at a given pressure $T_h(P) \propto [J - (P\delta V)]$ [6]. Note that $T_h(P) \propto J$ for $P=0$ and $T_h(P)=0$ for $P=J/\delta V$. The behavior of this simple model is described by the singularity free scenario [see Fig. 1(a)]. $T_h(P)$ (the temperature at which the correlation length related to the formation of a hydrogen bond network shows a maximum) must not be confused with $T_H(P)$ (the homogeneous nucleation temperature of real water). In water, the expected maximum at $T_h(P)$ is undetectable, because $T_h(P) < T_H(P)$.

However, by considering an internal correlation among the four hydrogen bonds formed by each single molecule, the scenario changes from singularity free to critical-point-like [6]. This internal degree of correlation in the water molecules is tuned by a new intramolecular term with energy $-J_\sigma$ added to the Hamiltonian of the liquid [6]. If $J_\sigma \rightarrow \infty$ the water molecule is always internally correlated for any value of the pressure and the thermodynamic functions show a discontinuity at $T_h(P)$ [see Fig. 1(c)].

The liquid-liquid critical point at T_c and P_c shows up when J_σ is finite and smaller than J . In this case, the water molecules are able to correlate themselves internally only if $T < T_*$, being T_* a pressure independent temperature proportional to J_σ . For $P < P_c$ the water molecules are not internally correlated at $T_h(P)$ [i.e. $T_h(P) > T_*$], the correlation length of the hydrogen bonds network cannot tend to infinity, and the response of the thermodynamic functions is nondivergent.

However, as the pressure increases $T_h(P)$ decreases. So, there is a critical value of the pressure $P = P_c$ where the water molecules are internally correlated at $T_h(P_c)$ [i.e., $T_h(P_c)$

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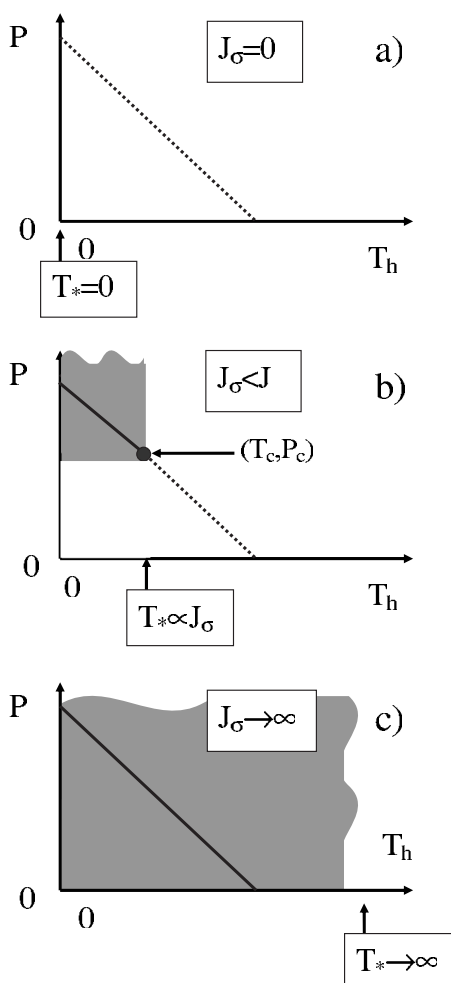


FIG. 1. Three possible scenarios depending on the value of J_σ . (a) If $J_\sigma=0$ there is no internal correlation in the water molecule for any pressure ($T_*=0$) and there is no long-range correlation in the formation of the hydrogen bonded network. The transition is always singularity free (dotted line). (b) If $J_\sigma < J$ and different from zero, there is long-range correlation in the transition to a low density liquid only when the transition temperature T_h is smaller than the temperature T_* corresponding to the internal correlation of the water molecules. In this particular case we obtain a critical point (T_c, P_c) and a first order phase transition for any pressure $P > P_c$ at a temperature $T_h < T_c \sim T_*$ (gray region and continuous line). (c) If J_σ is large enough compared to J there is always internal correlation in the water molecules for any pressure and the transition to a low density liquid is first order for any pressure (gray region and continuous line).

$\leq T_*$], the correlation length of the hydrogen bond network is capable of tending to infinity, and the response of the thermodynamic functions becomes divergent at $T_h(P_c) = T_c$. Of course, for any $P > P_c$, the four hydrogen bonds formed by any water molecule are internally ordered at $T_h(P) < T_*$ and the response of the thermodynamic functions becomes the one corresponding to a first order phase transition between two liquids with different density [see Fig. 1(b)]. Note how, by tuning the intramolecular term J_σ , we can easily change the physical mechanism of the simulated liquid form singu-

larity free ($J_\sigma=0$) to a liquid-liquid phase transition ($0 \neq J_\sigma < J$).

In real water, this intra-molecular term in the water molecule could be related to the value of the H-O-H angle. Experiments show that the relative orientations of the arms in the water molecule are correlated, with the average H-O-H angle equal to 104.45° in the isolated molecule, 104.474° in the gas, and 106° in the high- T liquid [7], suggesting an intramolecular interaction between the arms. This interaction must be finite because the angle changes with T , consistent with *ab initio* calculations [8] and molecular dynamics simulations [9].

Based on the model, we propose the following hypothesis [see Fig. 1(b)]: If there is a second critical point at P_c and we cool down the water deep into the supercooled region at constant $P > P_c$, internal correlation inside the water molecules at a temperature $T_* > T_h$ develops. The fluctuations in the energy of the system due to this intramolecular ordering process give rise to a maximum in the specific heat with the following characteristics: (i) it is located at a temperature $T_* > T_h$, (ii) it is nondivergent (because it is not due to the cooperative effect of many molecules but to the internal ordering of each molecule separately), and (iii) the position of the maximum is pressure independent (i.e., since the interaction J_σ does not induce any increase in volume, the value of T_* should be pressure independent).

On the other hand if $P < P_c$ and we cool down the liquid to T_h (with $T_h > T_*$) no secondary maximum appears in the specific heat (only the regular maximum attainable in numerical simulations but not in a real supercooled bulk water experiment). In the case of a singularity free scenario [Fig. 1(a)], where there is no critical point (critical pressure), no internal ordering in the water molecules takes place, and, independently of the pressure applied, no two maxima in the specific heat are found.

III. NUMERICAL RESULTS FOR THE MODEL

In order to test this hypothesis we have simulated the liquid phase of the model described in Ref. [6] by computing the total energy density of states $g(E)$ [10]. The algorithm is based on the following observation: If we perform a random walk in energy space with a probability to visit a energy level E proportional to $1/g(E)$, then a flat histogram should be generated for the energy distribution. Of course, at the beginning of the simulation, the true value of the energy density of states $g(E)$, i.e., the number of all possible states (or configurations) for an energy level E of the system, is unknown. So, we simply set all entries to $g(E)=1$ for all possible energies. This estimated density of states is then modified in a systematic way to produce a flat histogram over the whole range of energies, simultaneously making the density of states converge to the true value $g(E)$. We modify the density of states constantly during each step of the random walk and use the updated density of states to perform a further random walk in energy space. The modification factor of the density of states is also modified during the calculation and, at the end of the simulation, it should be very close to 1, which is the ideal case for the random walk with the true

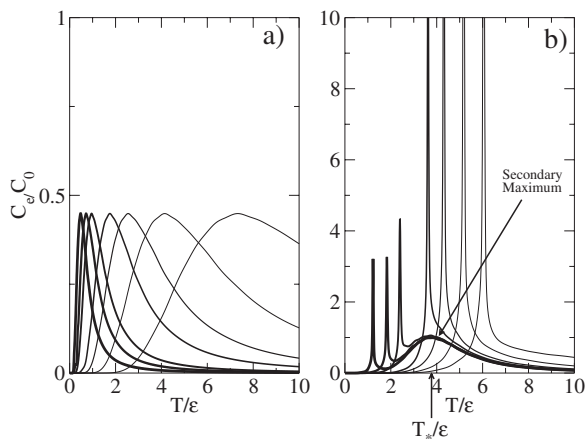


FIG. 2. Constant pressure specific heat vs temperature for different pressures $Pv_0/\epsilon=0.54$ (thinner line), 0.74, 0.84, 0.89, 0.94, 0.955, 0.97 (thicker line), and for (a) $J_\sigma/\epsilon=0$ (singularity free scenario) and (b) $J_\sigma/\epsilon=5$ (liquid-liquid critical point scenario). Note how we find secondary maxima only in (b) and for $Pv_0/\epsilon>0.89$, indicating that the critical pressure of the model must be close to $Pv_0/\epsilon=0.89$. The relative values of the maxima of the peaks are system-size dependent expect for the secondary peaks indicated in (b). Absolute specific heat values are normalized to C_0 , the value of the secondary maxima found in (b).

density of states. More details of the algorithm may be found in Ref. [10]. From the density of states we can estimate the specific heat by calculating canonical averages at any temperature. This algorithm is especially useful for models like the one presented in this paper, because all possible energy levels are visited with the same probability, overcoming the tunneling barrier between coexisting phases at first order phase transitions.

We have chosen the following values for the parameters: $J/\epsilon=50$ (ϵ being the value of the van der Waals interaction energy which in our case, since we consider only the condensed liquid phase, does not play any role) and $\delta V/v_0=50$ (being $100v_0$ the hard core volume of the water molecule). We choose these values taking into account that the average hydrogen bond interaction in water is close to 30 kJ/mol and that, in most molecular models of water, ϵ is set to 0.6 kJ/mol. Also, with these parameters, the ratio of the increment in volume due to the formation of a hydrogen bond, to the hard core volume of the water molecule considered has a physical value equal to 0.5.

We have performed two sets of calculations, one for a liquid with no liquid-liquid critical point ($J_\sigma/\epsilon=0$) and another one with a liquid-liquid critical point ($J_\sigma/\epsilon=5$). All other parameters are the same than in Ref. [6]. The behavior of energy fluctuations (constant pressure specific heat) has been calculated for a system of 225 water molecules with periodic boundary conditions and with the following values for the pressure $Pv_0/\epsilon=0.54, 0.74, 0.84, 0.89, 0.94, 0.955, 0.97$. Results are shown in Fig. 2.

Figure 2(a) gives the results for the model liquid with no-critical point. In this case no secondary maximum is found for any pressure. Figure 2(b) gives the results for the

model liquid with a critical point and a coexistence line between a LDL phase and a HDL phase. Note how the specific heat, for pressures $Pv_0/\epsilon>0.89$, has two maxima. The characteristics of the secondary peaks found are the following: they are located always at a temperature (T_*) greater than (T_h), they are nondivergent, and the temperature (T_*) is pressure independent. These findings agree with our previously presented hypothesis and suggest that there is a critical point at a pressure $Pv_0/\epsilon\sim 0.89$ for liquid (b).

There is a pertinent comment about the values of the main maxima of the specific heat shown in Fig. 2. Since we are dealing with a small system with finite size effects the concrete values of the maxima are not representative. For example, for the isothermal compressibility, it is found that maxima are proportional to the number of molecules in the first order phase transition, and that they scale as a power of the number of molecules when the transition is at the critical point (second order phase transition) [6]. In any case, they are not measurable in a real experiment due to the homogeneous crystallization of water. On the contrary, the secondary maxima shown on Fig. 2(b) are nondivergent. To check that they are nondivergent we have also studied the behavior of the secondary maxima for a different number of water molecules and we have found that they do not depend on the size of the system.

IV. THE EXPERIMENT IN REAL WATER

This nondivergent secondary peak found for $P>P_c$ could be measured in a real, high pressure, water experiment, since it is located at a temperature ($T_*\sim T_c$) above the nucleation temperature ($T_*>T_H$). The scheme of the concrete experiment to be performed is presented in Fig. 3. Calorimetric measurements on water should be performed for pressures ranging from the atmospheric value to approximately $P=2$ kbar in the supercooled region. Until now, calorimetric measurements in bulk water have been performed mainly at low pressures [11] and no maximum has been found down to $T=240$ K. However, according to our hypothesis, if there is a liquid-liquid critical point due to an internal correlation in the water molecule, calorimetric measurements should present a nondivergent maximum for values of the pressure $P>P_c\sim 1.7$ kbar [12] at a temperature T_* above the homogeneous nucleation temperature $T_H(P)$, located between 200 and 180 K, depending on the value of the pressure applied. The value of T_* should be almost pressure independent and close to the hypothesized critical temperature $T_c\sim 200$ K [12]. This maximum should not show up in other quantities such as the compressibility because the intramolecular term considered for the water molecule does not imply any change in volume. On the other hand, if the real scenario in water is singularity free there should be no maximum in the specific heat.

We summarize the conditions for the existence, or lack of it, of a liquid-liquid critical point, comparing between the behavior found for the model and the behavior expected for real water.

For the model. The condition for the existence of a second critical point is a specific heat with two maxima for $P>P_c$.

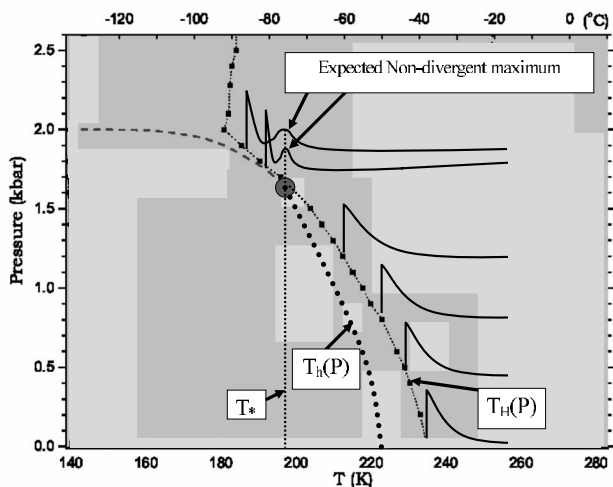


FIG. 3. Schematic representation of the experiment proposed to test the existence of a second liquid-liquid critical point at $P_c \sim 1.7$ kbar and $T_c \sim 200$ K (black circle). Constant pressure specific heat measurements should be performed by cooling down water until reaching the homogeneous nucleation temperature T_H (squares). For pressures smaller than ~ 1.7 kbar the specific heat should present the usual constant increase when cooling into the deeply supercooled region. But the expected maximum in the specific heat at T_h (circles) should be never reached. However, for larger pressures (in the range from 1.7 to 2 kbar), there should be a previous nondivergent maximum at $T=T_*$ (dotted line) and close to the temperature $T=200$ K independently of the pressure applied. This behavior for the specific heat has been schematically represented on the figure (thick continuous lines). Dashed line is the proposed coexistence line.

The first maximum is pressure dependent and the secondary maximum is pressure independent.

For the model. The condition for the nonexistence of a second critical point is a specific heat with a pressure dependent, single maximum for every pressure.

For real water. The condition for the existence of a second critical point is a single maximum for $P > P_c$. The maximum is pressure independent and it is located at a temperature above the homogeneous nucleation temperature, close to the hypothesized critical temperature.

For real water. The condition for the nonexistence of a second critical point is a specific heat for which no maximum can be reached at any pressure.

The difference between the different response of our model and that of real water is due to a lack of homogeneous nucleation in the model. For this reason, in the model proposed, we are able to detect the fluctuations due to the formation of the hydrogen bonded network and a pressure dependent specific heat maximum.

Recently, some very interesting calorimetric experiments have been performed on confined water. Confined water is not water under pressure; however there are some very important analogies. Confinement and pressure avoid homogeneous nucleation down to very low temperatures. For that reason, following the arguments presented on this paper, we should expect a nondivergent specific heat maximum in con-

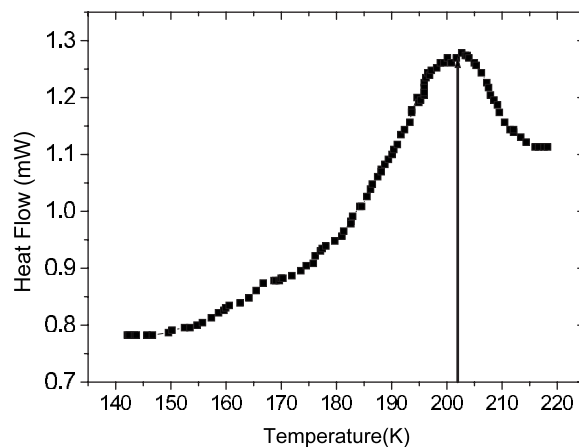


FIG. 4. DSC heating scans of hydrated purple membrane at low temperatures from Ref. [13]. Arrow marks the maximum at $T \sim 200$ K. This maximum could be related to the internal correlation in the water molecules responsible for the liquid-liquid critical point.

finned water at temperatures close to $T_c=200$ K, due to the internal ordering of the water molecule.

Actually, differential scanning calorimetric experiments (DSC) on water embedded in purple membranes [13] find a nondivergent maximum close to 200 K (see Fig. 4). Neutron diffraction did show that, upon heating to 200 K the intermembrane water space decreased sharply with an associated strengthening of ice diffraction, indicating that some water beyond the first membrane hydration layer flowed out of the intermembrane space to form crystalline ice. It was concluded that the confined water undergoes a glass transition at 200 K to adopt an ultraviscous liquid state capable of flowing out of the membrane and crystallizing to form ice. Authors argue that the DSC peak found at 200 K is most likely due to the possible glass transition. However, even if dynamical transitions at 150 and 260 K were found by studying the effects of the confined-water glass transition on nanosecond membrane dynamics, no dynamic transition was found at 200 K. Authors suggest that nanosecond membrane dynamics are not sensitive to the state of water beyond the first hydration layer. However, there is another possible way to explain this peak, based on the theory proposed in the present work: The maximum found at 200 K could be related, not to a particular dynamic transition, but to the internal correlation in the water molecules responsible for the liquid-liquid critical point. This possibility could be confirmed, or ruled out, by performing high pressure calorimetric experiments in supercooled water.

V. CONSTANT DENSITY NUMERICAL SIMULATIONS IN TIP4P-EW WATER

All results presented in this work are based on constant pressure measurements, in which the density changes by cooling down the system. However, what kind of behavior do we expect for the specific heat if the density of the system remains constant? In the simple model described in this

work, at the condensed liquid phase, changes in density are due to changes in the number of hydrogen bonds. If the density is constant, the number of hydrogen bonds remains also constant and energy fluctuations came mostly from the internal degree of freedom J_σ . So, at constant volume, the specific heat shows a single maximum at $T=T_*$ for any value of the density.

The TIP4P-Ew water model [14] reproduces the thermodynamic and structural properties of liquid water and of the different ice polymorphs well [15]. Recently, extensive constant density simulations on deeply supercooled TIP4P-Ew water have been performed [16]. In a molecular dynamics simulation of a full atom model of water such as the TIP4P-Ew, a constant volume simulation does not necessarily imply a constant number of hydrogen bonds when changing the temperature. Specific volume could remain constant when cooling down the system by slightly changing the hydrogen bonds equilibrium distance. If the number of hydrogen bonds increases by cooling down the system then the equilibrium distance must decrease. This change in equilibrium distance modifies the internal energy coming from hydrogen bonds and van der Waals interactions. However, for large enough densities, energy fluctuations coming from creation and annihilation of hydrogen bonds should be decimated. Basically, even a small increase in volume due to the formation of the hydrogen bonds network should not be admissible for large densities.

So, according to our hypothesis, at large enough densities, constant volume molecular dynamic simulations of the TIP4P-Ew model should present a single maximum in the specific heat, due to the constant volume internal ordering of the water molecules, at a constant temperature $T=T_*$ very close to the liquid-liquid critical temperature (T_c). To check this hypothesis we used internal energy data from Ref. [16] to compute the specific heat of TIP4P-Ew water at constant volume. Results are presented in Fig. 5. Note how a single maximum is found at a constant temperature $T_*=206$ K slightly above the critical temperature of the model $T_c \sim 200$ K for densities approximately above 1.1 g/cm^3 .

It is important to mention that the water molecule in the TIP4P-Ew model is rigid. In this case the internal degree of freedom responsible for the long range correlation between the water molecules cannot be due to the bending of the angle formed between the two hydrogen atoms. The internal degree of freedom could come from an orientational internal ordering among the water molecules which is not accompanied by any increase in volume.

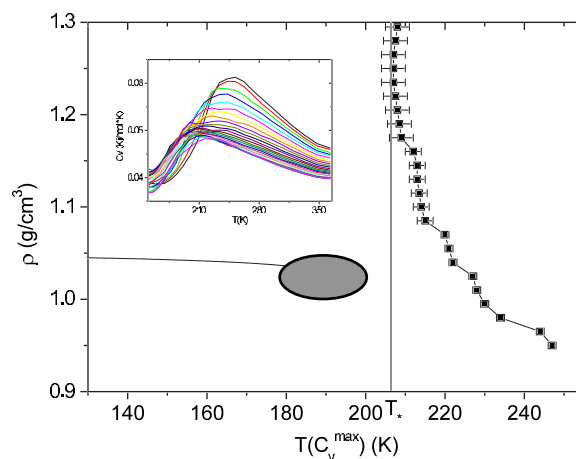


FIG. 5. (Color online) Temperature of the constant volume specific heat maximum vs density for the TIP4P-Ew water model. For densities above 1.1 g/cm^3 the maximum is fixed to $T=T_* \sim 210$ K (dashed line). Gray surface is the estimated critical region and dotted line is the estimated coexistence line. Note how T_* is located slightly above the critical region. Inset is the behavior of the specific heat for the different densities considered. Specific heat was calculated using internal energy data from Ref. [16].

VI. CONCLUSIONS

Based on results from a simple model we conclude that the existence of a liquid-liquid critical point at (T_c, P_c) due to an internal degree of freedom in the water molecules could be strongly supported by the existence of a nondivergent maximum in the water specific heat at high pressures. This maximum should be found at a constant temperature close to T_c for every pressure $P > P_c$. Preliminary results from water confined in nanoscopic environments, as well as constant density molecular dynamics simulations, seem to point toward the existence of this maximum.

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