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Temperature of maximum density line of a polarizable water model

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Monte Carlo simulations of liquid water were performed with a polarizable model in a narrow range of temperatures around the temperature of maximum density (TMD) and a broad pressure range, extended also to negative pressures. In order to infer features of the phase diagram relevant for the explanation of the anomalous behavior of water the pressure dependence of the TMD line was analyzed. The TMD is found to increase with decreasing pressure up to 274.8 K at −32 bar, and decrease upon further stretching. This behavior excludes the possibility of a reentrant liquid-gas spinodal line.

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Water is an extremely important substance in many areas of science. From the physical point of view the anomalous thermodynamic behavior makes it a peculiar liquid. The most evident anomalous feature is certainly the fact that at constant pressure its density goes through a maximum when the temperature is increased from the melting point [1,2]. Similarly, several other thermodynamic and dynamical properties show anomalous pressure or temperature dependence. For instance, upon isothermally increasing the pressure the translational diffusion coefficient goes through a maximum and the viscosity coefficient through a minimum [3]. Similarly, the isothermal compressibility [1] and heat capacity [2] exhibit a minimum as a function of the temperature. These thermodynamic response functions show anomalous behavior also in the supercooled liquid state, i.e., when decreasing the temperature they increase rapidly and either go through a maximum or diverge [4].

Several theories have been developed in the past decade to explain at a thermodynamic level the anomalous behavior of supercooled water. The singularity-free interpretation [5,6] assumes that upon isobaric cooling the thermodynamic response functions go through a maximum but remain finite. Another of these theories uses the assumption that two distinct liquid phases exist in the supercooled region [7,8]. The two phases are separated by a line of first order phase transitions, ending at a second critical point. This hypothesis is supported by two important findings. First, the two distinct supercooled liquid phases can be identified with the experimentally observed [9,10] low density amorphous and high density amorphous ice [7,8]. In this picture ordinary liquid water represents the supercritical state corresponding to this liquid-liquid phase transition. Second, even a simple system of spherical particles, interacting through an interaction potential consisting of a hard sphere repulsion, a linear repulsive shoulder, and a van der Waals attracting term, exhibits most of the anomalous properties of water and has also a liquid-liquid first order phase transition and critical point in the supercooled region [11].

An alternative explanation is the ‘‘stability limit conjecture’’ of Speedy and Angell [4,12], which assumes that the liquid-vapor spinodal line, representing the limit of existence of metastable liquid water, is not monotonic in the entire phase diagram. Instead, with decreasing temperature the spinodal pressure decreases up to a certain point below zero, where the spinodal curve changes slope and upon further decrease of the temperature becomes reentrant (i.e., enters back into the positive pressure range) in the deeply supercooled region of the phase diagram. Thus, limits of superheating, stress, and supercooling of liquid water are described here by one single spinodal line. The behavior of the spinodal curve is known to be closely related to the pressure dependence of the temperature at which the density of water attains a maximum along a given isobar (temperature of maximum density or TMD line). Thermodynamic arguments have shown that for any liquid having a TMD line only two types of thermodynamically consistent phase diagrams can be constructed. In the first case the TMD line increases monotonically with decreasing pressure and it ends at the intersection with the spinodal curve [13]. At this intersection the spinodal line goes through a minimum and becomes reentrant at lower temperatures [12,14]. The second scenario assumes that at a certain pressure the TMD line changes its direction, and upon further decrease of the pressure it starts to decrease. This type of TMD line cannot intersect the spinodal line [14], which consequently must decrease monotonically in the entire phase diagram. Therefore, the behavior of the TMD line can be conclusive for the relevance of the stability limit conjecture for water.

Any experimental test of the above hypotheses is strongly hampered by the fact that in both cases the important features of the phase diagram are located in extreme conditions (i.e., in deeply supercooled or negative pressure states), which cannot always be accessible. This fact enhances the importance of computer simulation methods, even if simulations can only be decisive for different water models, and provide only some hints about the phase diagram of real water. For instance, it has been demonstrated that the TMD lines of both ST2 [15] and TIP4P [16] water models change direction in the negative pressure region, and hence the stability limit conjecture does not provide an adequate phase diagram for these models [7,14]. Moreover, for ST2 water the existence of two distinct supercooled liquid phases has

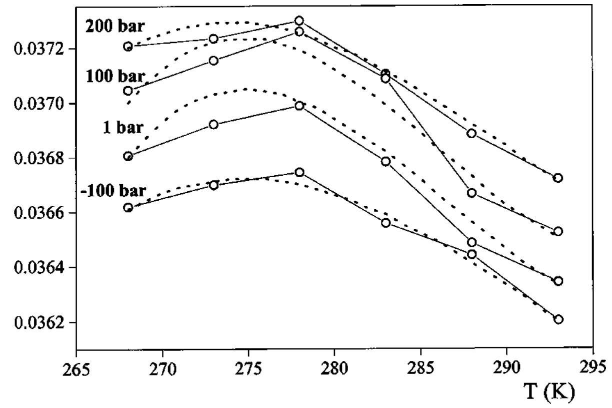

FIG. 1. Temperature dependence of the molecular number density of BSV water along four isobars, as obtained from Monte Carlo simulations (circles). The solid lines connecting the points are just guides to the eye. Constant pressure segments of the $\rho_m(T,p)$ surface fitted to the simulation data [see Eq. (1)] are shown as dashed lines.

been demonstrated and the location of the liquid-liquid critical point estimated [17]. However, these water models are known to inaccurately describe the behavior of water around the temperature of maximum density. Thus, at atmospheric pressure the temperature of maximum density of the ST2 model is about 50 K above the experimental value [7,14], whereas that of TIP4P appears in the deeply supercooled region at 255 K [18]. It is also known that ST2 strongly overestimates the tetrahedral coordination of the water molecules [19], a feature that plays a key role in the anomalous behavior of water.

In fact, the most widely used simple potential models of water are, in general, unable to reproduce the temperature of maximum density, even at atmospheric pressure. Thus, the density of the SPC [20] and TIP3P [16] models does not have any maximum in the entire temperature range of 223–373 K [18], whereas the temperature of maximum density of the SPC/E model [21] has been estimated as 235 [22] and 245 K [23] in two different ways. Although the recently developed TIP5P model [24] is claimed to well reproduce the TMD of water, at least at atmospheric pressure [24], this is only the case if the electrostatic interactions are neglected beyond a certain cutoff distance. On the other hand, when the long-range part of the electrostatic interactions is also taken into account the density maximum of this model is found to be at about 285 K [25]. On the other hand, potentials belonging to a more advanced group of water models, which account explicitly for the polarization of the molecules due to the local electric field, seem to do a much better job in reproducing the temperature of maximum density. The polarizable PPC [26] and BSV [27] models have been found to have their density maximum at 277 [28] and 278 K [29], respectively. Moreover, we have recently shown that the TMD of the BSV model agrees well, within about 2–3 K, with that of real water in the entire pressure range of its existence in thermodynamically stable liquid water [30]. This ability of the BSV model makes the investigation of the behavior of its TMD line at negative pressures an important issue.

In this paper we report the results of such an investigation. Computer simulations were performed in a wide pressure range, including negative pressures, in order to clarify whether the stability limit conjecture provides a correct description of the properties of this model. A detailed analysis of the thermodynamic properties of BSV water in this range of thermodynamic states is given elsewhere [30,31]. We have recently shown that, although the BSV model somewhat overestimates the density of water at ambient conditions, it can well describe the dependence of the thermodynamic [29–31], structural [32], and dynamical [33] properties at ambient conditions, as well as their temperature and pressure dependence in a wide pressure range around the temperature of maximum density. The only weak point of the model in this respect is that, similarly to other polarizable models [28,34], it overestimates the change of density with increasing temperature (i.e., the magnitude of the thermal expansion coefficient) [29,30,34]. However, this failure can even be advantageous for the purpose of the present study, as it can largely facilitate the determination of the temperature of maximum density by preventing the effect from being washed out by the numerical inaccuracy of the simulations.

Monte Carlo (MC) simulations of BSV water were performed in the isothermal-isobaric (N,p,T) ensemble with 256 molecules at four pressures (i.e., 200, 100, 1, and -100 bar) and six temperatures (268, 273, 278, 283, 288, and 293 K). The long-range part of the Coulombic interactions was estimated by the reaction field method. Details of the calculations have been given in a previous paper [30]. The densities were averaged over 40 000 sample configurations, separated by 256 particle displacement and 1 volume change step each. The averaging procedure required about a six week long run for each system on a single R10000 SGI processor.

The temperature dependence of the molecular number density ρ_m is shown in Fig. 1 along the four isobars studied. As is clear, the highest density value is obtained at 278 K at each pressure p, indicating that the TMD line of the BSV model has only a rather weak pressure dependence, as it remains in a temperature interval less than 5 K wide around 278 K in the entire pressure range studied. This result is in agreement with the experimental findings. In fact, calcula-

TABLE I. The a_{ij} parameters of Eq. (1), as obtained from fitting the simulated density values.

j	a_{0j} (bar^{-j})	a_{1j} (K^{-1} bar^{-j})	a_{2j} (K^{-2} bar^{-j})	a_{3j} (K^{-3} bar^{-j})
0	-293.577	$3.122\,58$	$-1.091\,60\times10^{-2}$	$1.269\,88\times10^{-5}$
1	$-1.024\,52$	$1.088\,01\times10^{-2}$	$-3.847\,19\times10^{-5}$	$4.530\,42\times10^{-8}$
2	$9.397\,47\times10^{-3}$	$-9.961\,76\times10^{-5}$	$3.516\,95\times10^{-7}$	$-4.135\,34\times10^{-10}$

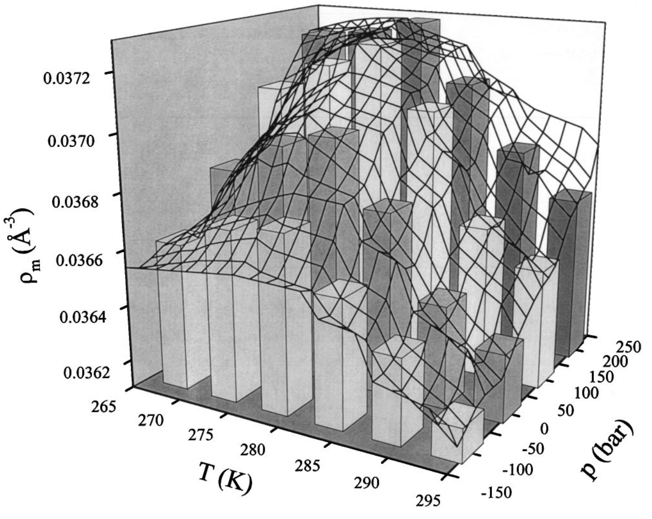

FIG. 2. Comparison of the simulated density values, shown as bars, with the $\rho_m(T,p)$ surface fitted to the simulation data [see Eq. (1)].

tions based on the Saul-Wagner equation of state [35], parametrized to the experimental properties of water in a broad pressure and temperature range, show that the temperature value corresponding to the maximum density of water falls between 271.5 and 277.2 K in the pressure range of 0–250 bar.

In order to analyze the temperature and pressure dependence of the density of the system and the behavior of the TMD line of the model in more detail we have fitted a polynomial function to the density values in the form of

$$\rho_m(T,p)=\sum_{i=0}^{3}\sum_{j=0}^{2} a_{ij}T^i p^j. \tag{1}$$

The a_{ij} parameters of the fitted function are summarized in Table I. Constant pressure segments of the fitted $\rho_m(T,p)$ surface are also plotted in Fig. 1. As is clear, the fitted functions reproduce reasonably well the temperature dependence of the simulated density data along all four isobars. The entire fitted $\rho_m(T,p)$ surface is compared with all the simulated density values in Fig. 2. The comparison confirms that the pressure and temperature dependence of the density of BSV water can indeed be described by the expression of Eq. (1), as the fitted surface covers the simulated data well. In order to better visualize the detailed shape of the fitted surface $\rho_m(T,p)$, it is shown in Fig. 3 as a color-coded contour plot. The temperature values at which the density is a maximum at a given pressure can be derived from Eq. (1) in a straightforward way, by solving the equation

$$\left(\frac{\partial \rho_m}{\partial T}\right)_p=\sum_{i=1}^{3}\sum_{j=0}^{2} i a_{ij}T^{i-1}p^j=0. \tag{2}$$

The TMD line obtained in this way is shown in Fig. 3, and is compared with the experimental curve in Fig. 4. As is clearly seen, the resulting TMD line changes slope at -32 bar and 274.8 K, and starts to decrease for further decrease of the pressure. Considering the thermodynamic arguments of Poole *et al.* [14] such a result indicates that the spinodal line of the model must be monotonic in the entire range of its existence, and hence, as in simple nonpolarizable water models [7,14,36] such as ST2, TIP4P, and TIP5P, even the phase diagram of the polarizable BSV model cannot adequately be described in terms of the stability limit conjecture.

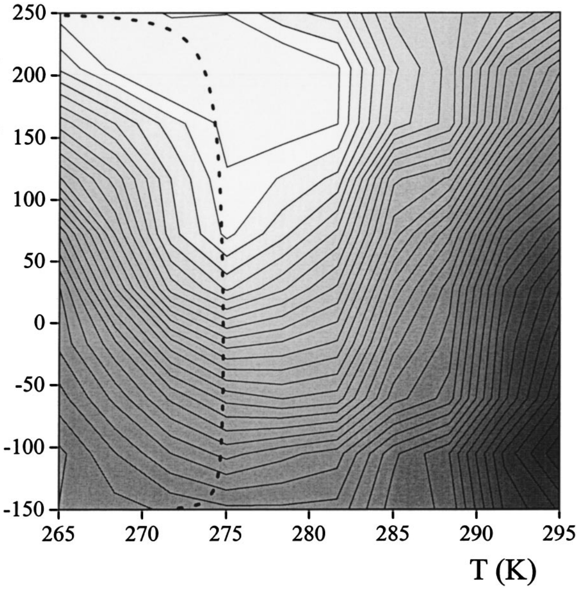

FIG. 3. Color-coded contour plot of the $\rho_m(T,p)$ surface fitted to the simulated density values [see Eq. (1)]. Lighter colors indicate higher densities. The TMD line, obtained from Eq. (2), is also shown as the dotted line.

In interpreting the above result two remarks are in order. First, one should be aware that, consistently with the density data obtained directly from the simulations, the TMD line resulting from the fitting procedure is almost (within 0.2 K)

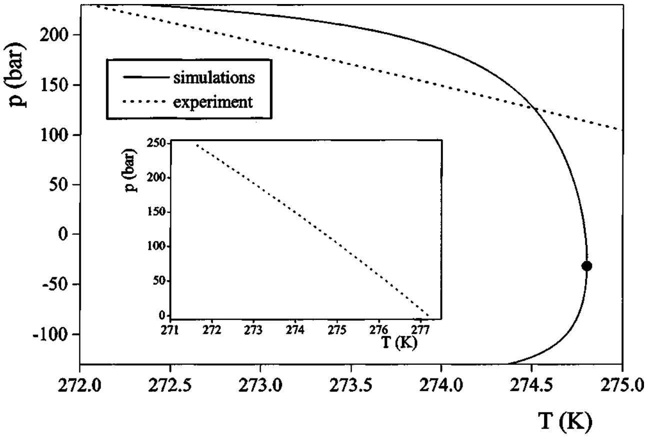

FIG. 4. Comparison of the TMD line of BSV water (solid line), obtained from Eq. (2), with the TMD line resulting from the Saul-Wagner equation of state [35], regarded here as "experimental" data (dashed line). The solid circle marks the (*T,p*) point at which the simulated curve changes the sign of its slope. The inset shows the experimental TMD line on a different scale, in the entire range of its existence at positive pressures.

constant in a rather broad (−100 to 100 bar) range of pressures. Therefore, the shape of the TMD line obtained is rather sensitive to the accuracy of the simulated density values. In order to demonstrate this we decreased the average density value obtained from the simulation at −100 bar and 268 K, i.e., 0.036 617 $Å^{-3}$, by its standard deviation value of 3.38×10^{-4} $Å^{-3}$. The TMD line recalculated using this modified data set is found to be monotonic in the entire pressure range simulated. The second point is that, as stated above, strictly speaking the present result is only valid for the BSV water model, and, although it makes it less likely, does not exclude completely the possibility of a phase diagram consistent with the stability limit conjecture for real water. Nevertheless, the comparison of the simulated and experimental TMD lines (see Fig. 4) allows us to make some deductions about the unknown, negative pressure behavior of the experimental curve. As is seen, the simulated curve reproduces the steepness of the experimental line at high pressures, whereas around 150 bar its steepness starts to decrease drastically. On the contrary, the experimental TMD line shows a roughly constant slope in the entire pressure range of 0–250 bar (see the inset of Fig. 4), and, according to recent experimental evidence also in the negative pressure range down to about −300 bar [37]. Assuming that (i) the experimental TMD line is indeed not monotonic either, and (ii) the simulated curve reproduces qualitatively the behavior of the experimental line, only being shifted in the *p*-*T* plane, we can conclude that the sudden decrease of the steepness of the experimental TMD line must occur at negative pressures, and the point where the sign of its slope is changed should be well below the simulated pressure value of −32 bar.

In conclusion, the present investigation demonstrated that a polarizable water model, which reproduces reasonably well the thermodynamic behavior of the system in a wide range of physical conditions, has a TMD line the shape of which is consistent both with the hypothesis that two distinct liquid phases exist in the supercooled region and with the singularity-free scenario, but inconsistent with the stability limit conjecture. In this respect the polarizable BSV model behaves similarly to the well known nonpolarizable ones. This is a relevant result, since it was obtained making use of a model potential which is more realistic in reproducing several thermodynamic and structural features of water. A comparison with the experimentally available data for the TMD line allows one to predict that in real water the limit of stability will extend to negative pressures even larger than those found for all the simulated systems.

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