

Simple Physical Explanation of the Unusual Thermodynamic Behavior of Liquid Water

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Here we demonstrate that the unusual thermodynamic behavior of water can be explained by a simple two-order-parameter Landau-type theory naturally and physically, without considering the effects of a liquid-liquid critical point. To describe the hydrogen-bonding effects on the phase behavior, we introduce a bond order parameter S , in addition to the density order parameter ρ . We ascribe the unusualness of water to the competing orderings of ρ and S , or their strong negative coupling. We argue that in usual liquids the crystallization is primarily a result of the ordering of ρ , while in water it is a result of the ordering of S at ambient pressure. [S0031-9007(98)06424-2]

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Liquid water exhibits unusual thermodynamic behavior, which is very much different from that of other liquids [1–6]. The most striking anomaly is the density maximum at 4°C and the decrease of the density upon its crystallization at 0°C. In addition, the isothermal compressibility K_T and specific heat at constant pressure C_P increase anomalously with decreasing the temperature [1,2,6–8]. It is widely believed that all the unusual features originate from special characteristics of hydrogen bonding. This seemingly slight extra complexity of water molecules makes the understanding of liquid water lag far behind that of other liquids, despite the fact that water is the most important liquid on the Earth.

To explain these unusual thermodynamic behavior of water, Speedy and Angell [7] proposed a new concept concerning supercooled water, which is known as “stability limit conjecture.” Later, a new amorphous form of water was found under a high pressure by Mishima *et al.* [9], which is suggestive of the existence of a liquid-liquid transition in water. Recent computer simulations and theories of water provide us with a new insight into this problem [2,5,10–13]: For example, the existence of a second critical point has been suggested, and its location in the pressure-temperature (P - T) phase diagram and its relation to the Speedy-Angell conjecture are argued [10–12,14]. However, there has so far been no consensus on the location of the additional critical point and even on its existence (see, e.g., [2,10,12]). This is partly because simulations are so sensitive to the choice of the intermolecular potential. A number of models free from the thermodynamic singularity [1,2], which ascribe the unusualness of water to second nearest neighbor (nonlocal) interactions [13] and cooperative hydrogen bonding [15,16], were also proposed. Although the thermodynamic properties of water have recently attracted much attention [2,3,17], they are still far from complete understanding, and the situation is quite confusing, as described above. For example, we still do not have any clear picture about what physical factors make water so unusual compared to

other ordinary liquids. The only consensus is the importance of hydrogen bonding.

In this Letter, we propose a simple model that provides an intuitive physical explanation of the anomalous thermodynamic behavior of water. We aim at seeking the physical origin that makes water so different from other ordinary liquids by developing a model that is not specified to water and can be applied to any liquids. We focus our attention on the effective attractive interaction potential between a molecule and its neighbors. It is generally given by the form $V(r, \Omega) = \bar{V}(r) + \Delta V(r, \Omega)$, where r is the distance from the center of mass of the molecule and Ω expresses the orientation. In water, the anisotropic part ΔV , of course, mainly comes from the hydrogen bonding. In general, thus, a liquid locally favors two different types of symmetry: one is favored by \bar{V} , maximizes density, and is consistent with long-range density ordering (the symmetry of crystal), while another is favored by ΔV and maximizes the number of local bonds. The symmetry of the latter is usually different from that of the former. In ordinary liquids, the local structure favored by ΔV is not consistent with any crystallographic symmetry. In water, however, it is consistent with the crystallographic symmetry of ice I_h . *The existence of these competing orderings causes energetic frustration*, which we believe plays key roles in vitrification of any liquids [18,19].

To express this complex feature of many-body interactions, we introduce two order parameters, ρ and S , representing density order favored by \bar{V} and bond order favored by ΔV , respectively. The ΔV leads to the formation of a locally favored hydrogen-bonded (HB) structure such as tetrahedral arrangement stabilized by active hydrogen bonds. The bond parameter S is, then, defined as the “local number density of locally favored HB structures”: $S(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$, where \mathbf{r}_i is the position vector of a locally favored HB structure (number i), which is randomly formed in space, and \sum_i is the sum about i over a unit volume around \mathbf{r} . The average value of S , \bar{S} , is

given by

$$\bar{S} = S_0 \exp[\beta(n\delta V - P\Delta v_S)], \quad (1)$$

where $\beta = 1/k_B T$ (k_B : Boltzmann's constant), since (i) a locally favored HB structure, which is stabilized by n hydrogen bonds, is in a lower energy state than the other part of the liquid by $n\delta V$ (δV : bonding energy) and (ii) it is destabilized by applying pressure P by $P\Delta v_S$, where Δv_S is the volume increase upon the formation of a locally favored HB structure.

The Hamiltonian of ideal liquids associated with only density fluctuations is given by [20]

$$\beta H_\rho = \int dr \left[\frac{\tau}{2} \delta\rho(\mathbf{r})^2 - \frac{a_3}{3} \delta\rho(\mathbf{r})^3 + \frac{a_4}{4} \delta\rho(\mathbf{r})^4 \right],$$

where $\tau = a_2(T - T_\rho^*)$ (T_ρ^* : the density ordering temperature) and $a_2, a_3, a_4 > 0$. Here $\rho = \bar{\rho} + \delta\rho$, where $\bar{\rho}$ is the average density and a decreasing function of T . In water, however, the bond order parameter plays essential roles in the freezing into ice I_h . The bond ordering can be expressed by the following free energy:

$$\beta H_S = \int dr \left[\frac{\kappa}{2} \delta S(\mathbf{r})^2 - \frac{b_3}{3} \delta S(\mathbf{r})^3 + \frac{b_4}{4} \delta S(\mathbf{r})^4 \right],$$

where $\kappa = b_2(T - T_S^*)$ (T_S^* : the bond ordering temperature), $S = \bar{S} + \delta S$, and $b_2, b_3, b_4 > 0$. By further adding the gradient terms and the relevant couplings between ρ and S to the above Hamiltonian of density ordering and that of bond ordering, we obtain the following Hamiltonian that we believe is relevant to the physical description of the phase behavior of water as well as other liquids:

$$\begin{aligned} \beta H_{\rho S} = & \beta H_\rho + \frac{K_\rho}{2} \int dr |\nabla \delta\rho(\mathbf{r})|^2 - \int dr \left[c_{1\rho} \delta\rho(\mathbf{r})S(\mathbf{r}) + c_{1S}\rho(\mathbf{r})\delta S(\mathbf{r}) + \frac{c_{2\rho}}{2} \delta\rho(\mathbf{r})^2 S(\mathbf{r}) + \frac{c_{2S}}{2} \rho(\mathbf{r})\delta S(\mathbf{r})^2 \right] \\ & + \beta H_S + \frac{K_S}{2} \int dr |\nabla \delta S(\mathbf{r})|^2. \end{aligned} \quad (2)$$

As explained before, S is frustrated with ρ . The above coupling terms represent the most significant effects of this frustration: an increase in S leads to a decrease in ρ and the density ordering temperature, while an increase in ρ leads to a decrease in S and the bond ordering temperature. Hence, all the coupling constants c_i in Eq. (2) should be negative. Because of these couplings, for example, the ordering temperatures, T_ρ^* and T_S^* , are shifted down to $T_\rho^{**} = T_\rho^* + (c_{2\rho}/a_2)\bar{S}$ and $T_S^{**} = T_S^* + (c_{2S}/b_2)\bar{\rho}$, respectively. This effect is physically the same as the "dilution effects" of impurities on spin ordering.

This Hamiltonian $H_{\rho S}$ well describes the basic features of the P - T phase diagram of water. In the P - T phase diagram of water (see Refs. [1,2]), the melting temperature of ice has a minimum around 2 kbar, which we call "crossover pressure P_x ." We argue that the primary order parameter of water is S below P_x (~ 2 kbar), while ρ above P_x . Thus, we identify the melting point of ice below P_x as $T_S^m = T_S^{**} + 2b_3^2/9b_2b_4$ [20] and that above P_x as $T_\rho^m = T_\rho^{**} + 2a_3^2/9a_2a_4$, respectively: The two melting curves, $T_S^m(P)$ and $T_\rho^m(P)$, cross with each other at P_x . Our model naturally explains the decrease of T_S^m (below P_x) and the increase of T_ρ^m (above P_x) with increasing P , as follows: (i) T_S^* and T_ρ^* , respectively, decrease and increase with increasing P , according to the Clausius-Clapeyron relation, since the specific volume increases and decreases, respectively, upon the ordering of S and ρ . (ii) With increasing P , $\bar{\rho}$ increases while \bar{S} decreases [see Eq. (1)] (note also that $c_{2\rho}, c_{2S} < 0$).

This provides us with a clear answer to the long-standing question why water is so unusual compared to all other liquids. We argue that the unusual features of the thermodynamic behavior of water originate from the fact that *the crossover pressure P_x is positive* ($P_x \sim$

2 kbar) *only in water while negative for all other ordinary liquids*. In water, thus, the crystallization at ambient pressure is primarily due to long-range bond ordering and not due to density ordering; namely, *the symmetry of ice crystal is selected mainly by ΔV , and not by \bar{V}* . This is consistent with the fact that the crystal structure of ice I_h [1] (a hexagonal "wurtzite" form) locally has the tetrahedral arrangement of oxygens preferred by hydrogen bonding, satisfying the constraint from a hard-core repulsion [21]. This can naturally explain the unusual phenomenon of the volume increase upon the freezing of water at ambient pressure, since the specific volume of a local structure favored by S is greater by Δv_S than that favored by ρ . In all other ordinary liquids, on the other hand, crystallization is induced primarily by long-range density ordering, although there exists the frustration with bond ordering. Thus, the density always increases upon crystallization. This picture is supported by the fact that in ordinary liquids $dT^m/dP > 0$ (T^m : melting temperature) for all positive pressures, while in water $dT^m/dP < 0$ below $P_x \sim 2$ kbar [1,2,6]. Figure 1 schematically shows the above difference between water and other ordinary liquids.

Next we discuss the unusual behavior of density on the basis of the Hamiltonian $H_{\rho S}$. Since the average values of ρ and S are shifted by their bilinear couplings, we redefine the fluctuations of ρ and S around their thermal equilibrium values, respectively, as $\delta\rho^* = \delta\rho - \langle\delta\rho\rangle$ and $\delta S^* = \delta S - \langle\delta S\rangle$, where

$$\langle\delta\rho\rangle \sim \frac{c_{1\rho}\bar{S}}{\tau - c_{2\rho}\bar{S}}, \quad \langle\delta S\rangle \sim \frac{c_{1S}\bar{\rho}}{\kappa - c_{2S}\bar{\rho}}. \quad (3)$$

The structure factor can then be obtained as

$$F(q) = \langle |\delta\rho_q^*|^2 \rangle = \frac{\kappa - c_{2S}\bar{\rho} + K_S q^2}{(\tau - c_{2\rho}\bar{S} + K_\rho q^2)(\kappa - c_{2S}\bar{\rho} + K_S q^2) - (c_{1\rho} + c_{1S})^2} \cong \frac{\xi^2}{K_\rho(1 + q^2\xi^2)}, \quad (4)$$

where $\xi^2 \sim \frac{K_\rho}{\tau - c_{2\rho}\bar{S}}$. Here we should regard $\tau - c_{2\rho}\bar{S}$ as a constant due to the first-order nature of the transition, which is quite consistent with the absence of the anomaly in the correlation length ξ [22].

For water and any other liquids, thus, we have the following relation for density [see Eq. (3)]:

$$\rho(T) \cong \bar{\rho} + \langle \delta\rho \rangle \sim \bar{\rho} - A_\rho \exp[\beta E_{\text{bond}}(P)], \quad (5)$$

where $E_{\text{bond}}(P) = n\delta V - P\Delta v_S$ and $A_\rho > 0$. Figure 2 shows the fitting of Eq. (5) to the density measured experimentally [6,23]. Here we use $\bar{\rho} = \rho_0 - \alpha T - \gamma T^2$. The agreement is quite satisfactory. The value of E_{bond} ($= 1800$ K) obtained by the fitting is quite reasonable because the hydrogen-bonding energy δV is estimated as $\sim 250\text{--}600$ K [1,5] and $n \sim 4\text{--}8$ for the proposed locally favored structures of water such as tetrahedral and larger polyhedral arrangements [1,2,5,22].

This behavior can be qualitatively explained as follows: Without bond formation, ρ always increases with decreasing T , due to van der Waals attractions. However, the increase in S upon cooling leads to the decrease in ρ . Bond ordering starts to overcome density ordering since the temperature dependence of the former is much stronger than that of the latter. This competition is primarily responsible for the unusual decrease in ρ upon cooling below 4°C in water. In usual liquids, on the other hand, density ordering always beats bond ordering due to small A_ρ and E_{bond} . Accordingly, the density of ordinary liquids monotonically increases with decreasing T . This difference originates from the fact that $P_x > 0$ for water, while $P_x < 0$ for all other liquids, as explained before. For the case of $P_x < 0$, bond ordering is always hidden by density ordering ($T_\rho^m \gg T_S^m$). However, it should be noted that if P_x is only slightly negative, the strong effects of the local bond ordering should still cause the similar phenomenon of a density maximum. This should be the case of SiO_2 [2,3].

The isothermal compressibility associated with density fluctuations, δK_T can also be calculated using Eq. (4) as $\delta K_T \sim \beta/(\tau - c_{2\rho}\bar{S}) \sim \beta K_\rho \xi^2$, under the Gaussian approximation. However, the absence of the anomaly of

the correlation length ξ (due to the first-order nature of the transition) indicates that the anomaly of K_T or C_P does not primarily originate from density fluctuations [22], in contrast to the Speedy-Angell conjecture [7] or the model based on a new critical point [10].

What is then the origin of the anomalous behavior of K_T and C_P ? It may be caused by the direct contribution of locally favored HB structures to K_T and C_P . The local compressibility and heat capacity of a locally favored HB structure should be larger than those of a non-hydrogen-bonded structure simply due to the soft nature and the additional vibrational entropy of the former, respectively. To confirm this picture, we fit the following functions to K_T and C_P , using the fact that the number density of locally favored HB structures is given by \bar{S} ,

$$K_T = \bar{K}_T + \bar{S}\Delta K_T = \bar{K}_T + A_K \exp[\beta E_{\text{bond}}(P)], \quad (6)$$

$$C_P = \bar{C}_P + \bar{S}\Delta C_P = \bar{C}_P + A_C \exp[\beta E_{\text{bond}}(P)], \quad (7)$$

where \bar{K}_T and \bar{C}_P are the background parts dominated by density order parameter, ΔK_T and ΔC_P are the increases in K_T and C_P upon the formation of a locally favored HB structure, respectively, and $A_K, A_C > 0$. We assume that \bar{K}_T and \bar{C}_P are quadratic and linear functions of T , respectively. As shown in Figs. 3 and 4, the above relations can reproduce the behavior of K_T and C_P quite well, with very reasonable backgrounds and more importantly the same value of E_{bond} as that used in the fitting of ρ . These excellent fitting results for the three physical quantities, ρ , K_T , and C_P (see Figs. 2–4), cannot be accidental, which strongly supports the validity of our model. We stress that all these anomalies can be commonly expressed by the extremely simple functional form of \bar{S} , namely, $\exp(\beta E_{\text{bond}})$ with the common value of $E_{\text{bond}} = 1800$ K. To our knowledge, this functional form of the anomaly is the simplest one among those ever proposed [1,2,15]. Here it is worth noting that Sasty *et al.* [16] showed that the anomalous behavior of K_T is a natural thermodynamic consequence of the volume expansion upon cooling, which is consistent with our picture.

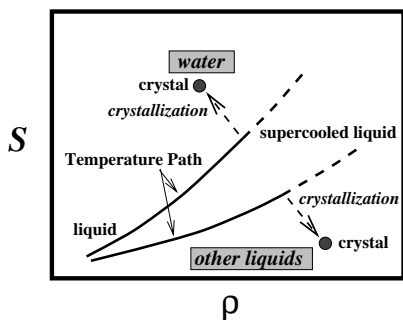


FIG. 1. The basic difference in the behavior in the (ρ, S) space between water at $P < P_x$ and ordinary liquids.

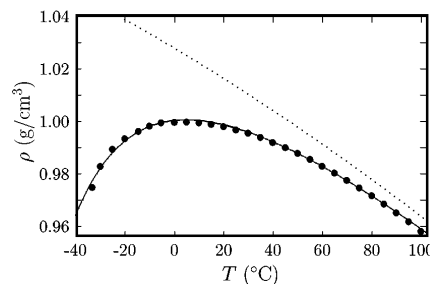


FIG. 2. Temperature dependence of the density of water [6,23]. The solid curve is the curve fitted by our theory with $E_{\text{bond}} = 1800$ K. The dotted curve is the background part.

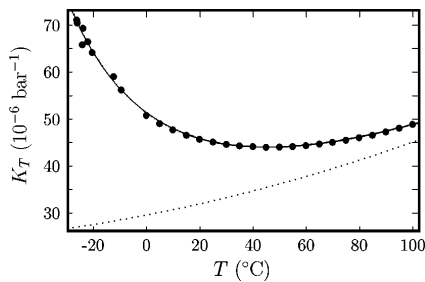


FIG. 3. Temperature dependence of K_T of water [6,7]. The curves have the same meanings as those in Fig. 2.

Our model further provides us with a natural explanation for the following facts: (i) With increasing P , the anomalous decrease of ρ upon cooling becomes less pronounced and the liquid temperature of maximum density (TMD) decreases [1,2]. (ii) The anomaly of K_T and C_P becomes monotonically weaker with increasing P and almost disappears under very high pressure ($P \gg P_x$) [8]. These behaviors can commonly be explained by the decrease in \bar{S} with increasing P [see Eq. (1)]: The decrease in \bar{S} with increasing P weakens the density anomaly and leads to the decrease in TMD [see Eq. (5)]. It also weakens the anomaly of K_T and C_P with increasing P [see Eqs. (6) and (7)].

In summary, we demonstrate that our two-order-parameter Landau theory of water naturally and consistently explains (i) the unusual behavior of ρ , K_T , and C_P including their pressure dependence, (ii) the volume increase upon freezing below P_x , (iii) the basic features of the P - T phase diagram of water (the pressure dependence of T^m), and (iv) the pressure dependence of TMD. Our theory leads to the following extremely simple scenario of the anomalous thermodynamic behavior of water: *The anomaly of ρ , K_T , and C_P is primarily due to neither thermodynamic singularity [7,10–12] nor cooperativity of hydrogen bonding [15,16], but due to the coupling between density and bond order parameters.*

In contrast to previous theoretical models of water [1,11,13,15,16], which are rather specific to water, our model is the first Landau-type theory of water, to our knowledge, that focuses on the competing orderings, namely, the frustration between density and bond ordering. Thus, our model can describe the basic thermodynamic behavior of not only water but also any other liquids [19] and, thus, naturally explains what physical factor

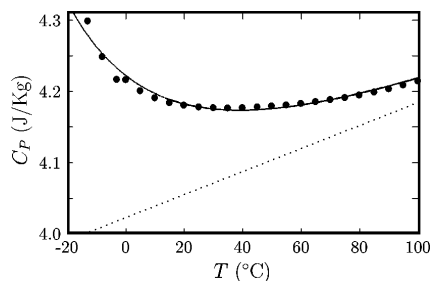


FIG. 4. Temperature dependence of C_P of bulk water [6,8]. The curves have the same meanings as those in Fig. 2.

makes water so different from other ordinary liquids. The unusual behavior of silica (SiO_2) similar to that of water such as the existence of TMD in a supercooled state [2,3] can also be explained by assuming a very weakly negative P_x for silica, which is consistent with the known P - T phase diagram of silica. Finally, we stress that our two-order-parameter model can be relevant even to the physical description of ordinary liquids in which $P_x < 0$: For $P_x < 0$, the hidden bond ordering can be regarded as the source of random disorder against density ordering, which causes the “spin-glass” effects and leads to vitrification [19]. Stronger frustration leads to stronger disorder effects. This answers the long-standing open question of what physical factor determines the fragility of liquids [3]. Our model tells us that a liquid having weaker frustration between ρ and S , namely, smaller (more strongly negative) P_x , is more fragile [19].

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