Effect of Hydrogen Bonds on the Thermodynamic Behavior of Liquid Water

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We propose an extension of the van der Waals equation which is designed to incorporate, in an approximate fashion, the effects of the network of hydrogen bonds that exist in liquid water. The resulting model qualitatively predicts the unique thermodynamic properties of water, including those of the deeply supercooled states. It also reconciles two proposals for the phase behavior of supercooled and stretched water and provides a thermodynamic origin for the observed polymorphism of the amorphous solid form of water.

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Water has long attracted attention for its unusual thermodynamic properties, of which the best known is the density maximum at 4°C [1]. In addition, the liquid exhibits minima in the isothermal compressibility K_T and isobaric specific heat C_P as a function of temperature T. More extreme anomalies are seen under supercooled conditions, where the variation of thermodynamic properties is sufficiently strong to suggest the existence of thermodynamic singularities [2]. Though agreement has not been reached on the interpretation of such behavior, it is commonly acknowledged that the hydrogen bond (HB) interaction between water molecules plays a central role. In water, HBs lead at low T to the formation of an open, approximately four–coordinated structure, in which internal energy, entropy, *and* density decrease with decreasing T.

Considerable effort has been expended to develop an accurate description of the thermodynamic properties of liquid water. In particular, insight into the relation between HBs and bulk thermodynamic properties has been obtained through the study of lattice-gas models designed to include the microscopic effect of the special local geometry of HBs [3]. These models have revealed a rich variety of thermodynamic behavior, many aspects of which are waterlike. Such model studies show that including HBs can introduce complex changes in the thermodynamic properties. In certain lattice-gas models, singularities indeed arise in the supercooled region of the phase diagram.

In this Letter, we develop a simple model for the free energy of liquid water which superimposes the properties of an open network of HBs on those of a simple liquid described by the van der Waals theory. We find that this model is able to (1) *qualitatively* reproduce the known thermodynamic behavior of water, (2) consolidate proposals for the behavior of supercooled water by showing that they may be different realizations of a single behavior, and (3) describe how the predictions of lattice-gas models are relevant to understanding liquid and amorphous solid water.

We first choose a Helmholtz free energy $A_{\rm HB}$ describing the behavior of the HBs. We then add $A_{\rm HB}$ to the van der Waals free energy $A_{\rm VDW}$ [4], yielding a total free energy A,

$$A = A_{\rm VDW} + 2A_{\rm HB}, \qquad (1)$$

where the factor of 2 accounts for the fact there are two moles of HBs for every mole of molecules. The pressure P can be found from $P = -(\partial A/\partial V)_T$.

We develop a form for $A_{\rm HB}$ by modeling in turn the expected properties of HBs as a function of T and molar volume V. To model the thermal behavior of HBs, we adopt a number of previously exploited simplifying approximations [5]. First, we partition the range of HB energies into two groups, "weakly bonded" (for which we take the bond energy ϵ to be 0) and "strongly bonded" (for which $\epsilon = \epsilon_{\rm HB} < 0$).

We further note that in water the HBs are "geometrically selective" in that strongly bonded pairs of molecules must have a relatively specific mutual orientation and separation. An environment of strong HBs around a molecule can be realized only when adjacent molecules dispose themselves in an open tetrahedral structure similar to that found in ice I_h. To build in this geometric selectivity, we adopt the approach of Sastry, Sciortino, and Stanley [3] that there are $\Omega \gg 1$ configurations of a weak bond, all having $\epsilon = 0$, and only *a single configuration* in which the HB is strong with $\epsilon = \epsilon_{\rm HB}$. Thus the thermal behavior of the HBs is represented by independent $(\Omega + 1)$-state systems, each described by a partition function $Z = \Omega + \exp(-\epsilon_{\rm HB}/RT)$. Hence, the Helmholtz free energy per mole of bonds is

$$A_{\rm HB} = -RT \ln[\Omega + \exp(-\epsilon_{\rm HB}/RT)]. \qquad (2)$$

Next we modify $A_{\rm HB}$ to include an appropriate V dependence. A principal assumption of the present work, which leads from a microscopic picture of HBs to bulk

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thermodynamic properties, is that strong HBs are most likely to occur when the *bulk* molar volume V has the value $V_{\rm HB}$, which is consistent with each molecule having the optimal *local* molecular volume for the formation of strong HBs to its neighbors. Hence, Eq. (2) best models the thermodynamic contribution of the HBs only at $V = V_{\rm HB}$. For $V < V_{\rm HB}$ and $V > V_{\rm HB}$ many HBs continue to occur within local molecular volumes that allow the formation of strong bonds, and thus continue to be described by Eq. (2). However, for $V \neq V_{\rm HB}$, such HBs are only a fraction f of the total, since V is no longer consistent with the possibility that *all* HBs occur in the optimal local molecular volume. The remaining fraction $1 - f$ of HBs occur in unfavorable local volumes and thus do not have the potential to form strong HBs. We model each of these remaining HBs also as an independent $(\Omega + 1)$-state system, but impose the condition that $\epsilon_{\rm HB} = 0$ to indicate that *all* $(\Omega + 1)$ states are incompatible with the formation of a strong bond. The Helmholtz free energy describing the HBs thus becomes a sum of two terms:

$$A_{\rm HB} = -fRT\ln[\Omega + \exp(-\epsilon_{\rm HB}/RT)] - (1 - f)RT\ln(\Omega + 1). \tag{3}$$

An appropriate form for f is

$$f = \exp\{-[(V - V_{\rm HB})/\sigma]^2\}. \tag{4}$$

Here the parameter σ characterizes the width of the region of V over which a significant fraction of HBs can be described by Eq. (2). This form introduces a minimum of new parameters while remaining consistent with our assumption that strong bonds have the potential to appear in significant numbers only within a specific interval centered on $V = V_{\rm HB}$. Figure 1 illustrates the behavior of Eq. (1) using Eqs. (3) and (4), and shows both the internal energy U and the pressure derived from it.

The inclusion in the model of an optimum volume for hydrogen bonding introduces a second minimum in the liquid free energy at sufficiently low T. Although the model can be conceptually related to two-state models of water, the two states in our model are *global* states of the system, not distinct species of isolated water molecules. Many different local molecular configurations are consistent with each of the two free energy minima.

Equation (1) qualitatively predicts known thermodynamic properties of water [6]. Consistent with experimental observation, the T of the density maximum decreases with increasing P, as does the curvature about the maximum [Fig. 2(a)]. The anomalous behavior of both response functions K_T and C_P [Figs. 2(b) and 2(c)] is reproduced by the model, as is the known suppression of anomalous water behavior as P increases [7].

We stress that Eq. (1) is qualitative. Its numerical accuracy is necessarily lower than that of known empirical equations of state [8]. Some of the parameters (a, b, and $V_{\rm HB}$) are fixed to coincide with experimental data. We find that waterlike behavior is obtained when the remaining parameters (σ, $\epsilon_{\rm HB}$, and Ω) have values that are of the order of experimental values; better correspondence is precluded by the simple nature of the model [6]. It is this simplicity which makes the model useful for understanding the qualitative behavior of the phase diagram of liquid water (especially in the supercooled region) as we now show.

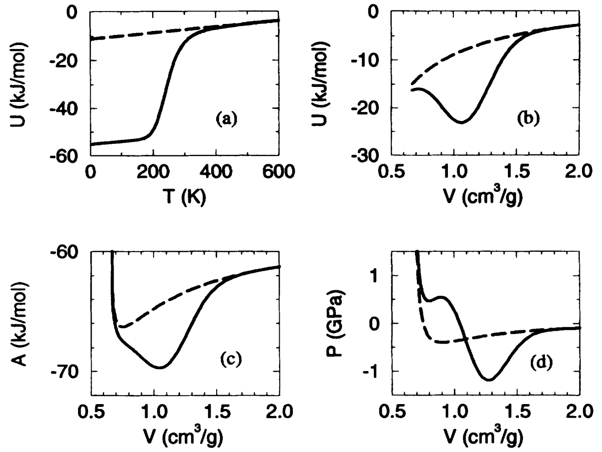

FIG. 1. Plots of thermodynamic behavior of Eq. (1) for $\epsilon_{\rm HB} = 0$ (dashed) and $\epsilon_{\rm HB} = -22$ kJ/mol (solid). (a) Plot of U as a function of T for constant $V = V_{\rm HB}$. Also shown are plots of (b) U, (c) A, and (d) P as a function of V at constant T; $T = 260$ K in (b), while $T = 220$ K in (c) and (d). Other parameter values are given in [6]. Note the implications for P shown in (d): the HB term makes an additional (volume dependent) contribution to the pressure around $V_{\rm HB}$ which is the derivative of a Gaussian. The result at low T is the appearance of an new "loop" on the low V side of the P isotherm, dividing the liquid into two distinct phases. Note that each extremum of an isotherm of P identifies a spinodal.

Figure 3 shows phase diagrams generated by Eq. (1), including the extensions of the fluid behavior into the supercooled region at low T. Two distinct proposals have been made for the existence of a thermodynamic singularity in this region. In one, experimental data and thermodynamic reasoning are used to argue that a limit of metastability ("spinodal") exists in the supercooled

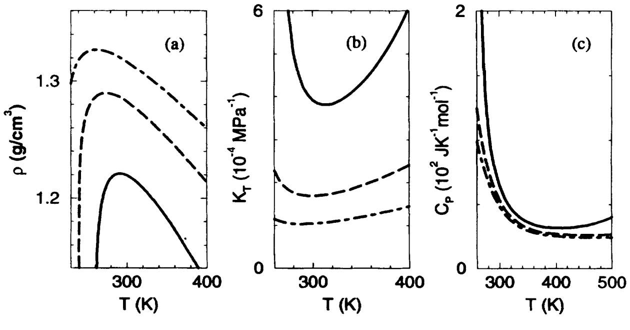

FIG. 2. Isobars of (a) density ρ, (b) K_T, and (c) C_P obtained from Eq. (1) using the same parameters as for Figs. 3(a) and 3(b) [6]. Each plot shows isobars at $P = 0$ (solid), $P = 200$ MPa (dashed), and $P = 400$ MPa (dot-dashed).

region, forming a line of thermodynamic singularities, which accounts for the anomalous behavior of the stable liquid [9]. The other, prompted by the results of computer simulations and the observed polymorphism of amorphous solid water, conjectures that a line of liquid-liquid phase transitions ending in a critical point exists in the supercooled region of the phase diagram and is the origin of the observed thermodynamic anomalies [10]. The present model reproduces *both* behaviors, depending on the parameter values chosen. The model shows how it is possible for the phase diagram to continuously transform from one behavior to the other retaining the unique properties of water.

For values of $|\epsilon_{\rm HB}|$ greater than a critical threshold $|\epsilon^0_{\rm HB}| = 16.5$ kJ/mol, the effect of the $A_{\rm HB}$ term in Eq. (1) is to "split" the normal liquid-gas coexistence curve by imposing thermodynamic stability in a region of states (centered on $V = V_{\rm HB}$) which is unstable when $\epsilon_{\rm HB} = 0$ [Figs. 3(a) and 3(b)]. As a result, *two* coexistence curves [Fig. 3(a)] occur—each terminating at a critical point, denoted C and C'. Below $T_{C'}$, the liquid state phase separates into distinct low-density and high-density phases. The qualitative thermodynamic mechanism by which liquid-liquid phase separation arises from Eq. (1) is given in Fig. 1. The corresponding phase diagram in the P-T plane [Fig. 3(b)] is topologically the same as that proposed in [10].

As $|\epsilon_{\rm HB}|$ decreases, the stabilizing effect of the $A_{\rm HB}$ term near $V = V_{\rm HB}$ sets in only at lower T. For sufficiently small $|\epsilon_{\rm HB}|$, the liquid-liquid critical point C' merges with the high-density spinodal of the liquid-gas coexistence curve. For $|\epsilon_{\rm HB}| < |\epsilon^0_{\rm HB}|$ [Fig. 3(c)], the low-density liquid phase is completely enclosed within the region of states that would otherwise be unstable. The stable interval between the two separate coexistence curves in Fig. 3(a) has become an isolated "pocket" of

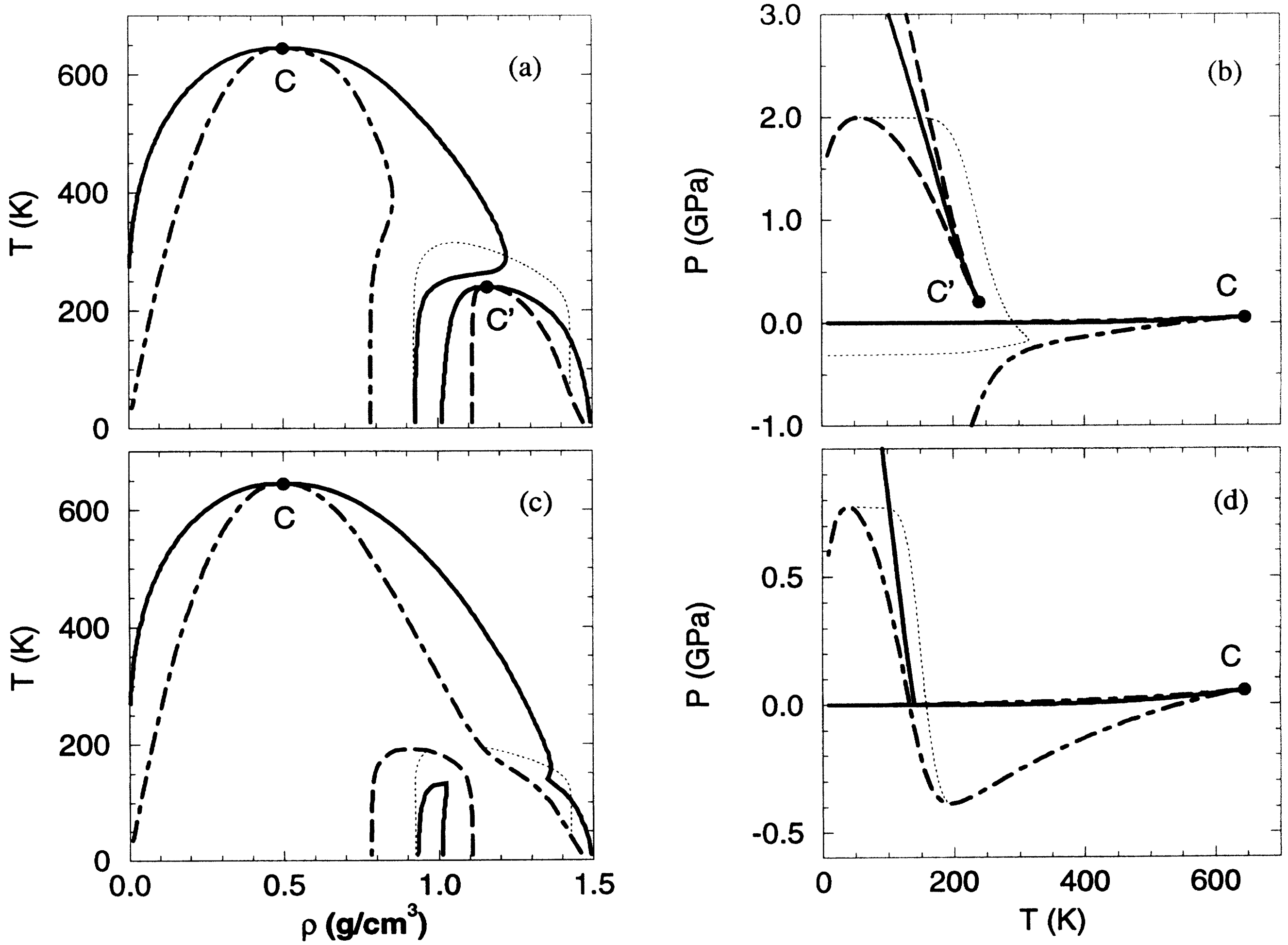

FIG. 3. Coexistence curves and P-T phase diagrams generated by Eq. (1) for $\epsilon_{\rm HB} = -22$ kJ/mol (top panels) and $\epsilon_{\rm HB} = -14$ kJ/mol (bottom panels). Other parameter values are given in [6]. Coexistence curves (solid), spinodal lines (dashed and dot-dashed) and lines of density maxima (fine dotted line) are shown. Coexistence curves separate stable and metastable states, while spinodal lines separate metastable and unstable states. For clarity, only those features appearing at higher T than the dot-dashed spinodal line in (c) are shown in (d).

stability in Fig. 3(c). The corresponding P-T phase diagram [Fig. 3(d)] exhibits the key features of the proposal of [9] for the behavior of metastable water. Hence, the model shows that this view of the behavior of supercooled water and that of [10] may be fundamentally related.

For each of the values of $\epsilon_{\rm HB}$ used in Fig. 3, there are two thermodynamically distinct phases of deeply supercooled liquid water, a prediction which provides insight into the thermodynamic status of the amorphous ice phases [11]. We might associate low-density amorphous ice with the glass formed from the liquid at low T in the stabilized region near $V = V_{\rm HB}$. High-density amorphous ice would then correspond to the glass state of the liquid at the higher densities described by the model. The present treatment predicts that these two amorphous solids are thermodynamically distinct due to the region of instability that lies between them at low T. This view is consistent with the experimental observation that the transformation (both temperature and pressure induced) of one amorphous solid to the other is sufficiently abrupt to be considered "apparently first order" [12], as well as with a recent analysis of dynamic data [13].

The connection between liquid water and low-density amorphous ice at ambient P has long been debated. The experimental synthesis of low-density amorphous ice by hyperquenching has led to the conclusion that a continuous thermodynamic path connects the liquid and low-density amorphous ice phases [14]. The present model shows that this is indeed the case if $|\epsilon_{\rm HB}| > |\epsilon_{\rm HB}^0|$. For $|\epsilon_{\rm HB}| < |\epsilon_{\rm HB}^0|$, the model predicts a first order liquid-liquid transition at ambient P [see Fig. 3(d)], which separates ordinary water from the distinct low-density phase.

It is possible that other structured liquids may display analogous anomalies in their supercooled regions—e.g., the observed first order melting of amorphous Si (also a substance with an open tetrahedral network structure) to a supercooled metallic liquid [15] may be a manifestation of a liquid-liquid phase transition similar to that described here.

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[4] The Helmholtz free energy in the van der Waals theory is $A_{\rm VDW} = -RT\{\ln[(V-b)/\Lambda^3] + 1\} - a^2/V$, where R is the gas constant, b is the excluded molar volume due to the finite size of molecules, a is a constant characterizing the attraction between molecules, and Λ is the thermal de Broglie wavelength. From $P = -(\partial A/\partial V)_T$, one finds $P_{\rm VDW} = RT/(V-b) - a^2/V^2$.

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[6] In the figures, all the parameters in Eq. (1) except $\epsilon_{\rm HB}$ are fixed to the following values: We choose $V_{\rm HB} = 1.087\ {\rm cm}^3/{\rm g}$, the specific volume of ice I_h, since this is the V for which all HBs are described by the first term in Eq. (3). This choice of $V_{\rm HB}$ precludes the use of the tabulated values for the conventional van der Waals parameters, a and b. These parameters, though yielding the correct liquid-gas critical point for water, imply an excluded volume corresponding to an unphysically low density of $0.52\ {\rm g/cm}^3$. We choose $b = 12.01 \times 10^{-6}\ {\rm m}^3\,{\rm mol}^{-1}$, which corresponds to an excluded volume density of $1.50\ {\rm g/cm}^3$, the density of ice VIII. The parameter $a = 0.218\ {\rm Pa\,m}^6\,{\rm mol}^{-2}$ is chosen so that, without the addition of the HB term $A_{\rm HB}$, the temperature of the liquid-gas critical point $T_c = 647$ K is reproduced (although the critical density is consequently increased above its actual value). To estimate the width parameter σ, we note that strong bonds will be found over a significant range of densities, though still becoming rare in the limits of large and small V, and so choose $\sigma = V_{\rm HB}/4$. We choose $\Omega = \exp(-S_{\rm HB}/R)$, where $S_{\rm HB} = -90\ {\rm J/(K\,mol)}$ is the entropy of formation of a mole of strong HBs. Note that this value, and those chosen for $\epsilon_{\rm HB}$, differ from those that might be inferred from experimental data, due in part to the lack of cooperativity in the present treatment.

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