

# On Possible Interpretations of the Anomalous Properties of Supercooled Water

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A search for ways to estimate thermodynamic properties of deeply supercooled water was undertaken to make it possible to analyze nucleation rates in droplets freezing in supersonic flow. It was found that the well-known anomalous behavior of supercooled water can be accounted for by the so-called “two-state” model that had been discredited 2 decades ago. The model was found to be viable when applied in a form closely related to one introduced by Speedy [*J. Phys. Chem.* **1984**, 88, 3364]. Water is apportioned into equilibrium concentrations of high- and low-density components in somewhat the same way as described recently by Vadamuthu *et al.* [*J. Phys. Chem.* **1994**, 98, 2222] except that criteria were imposed whereby the equilibrium constant inferred from the distribution was forced to obey the van’t Hoff temperature and Gibbs–Poynting pressure relations. It was found that the expansivity, heat capacity, and compressibility anomalies calculated by the model agreed well with those measured experimentally when the equilibrium was considered to be between relatively densely packed monomers and bulky aggregates containing five or six molecules. The model does not preclude a broader distribution of oligomers, particularly when the larger species are somewhat less bulky than the model pentamers and hexamers. An appealing feature of the model is that its results can be extrapolated to arbitrarily low temperatures, making it possible to estimate the heat and free energy of the freezing of water at the very low temperatures achieved in a supersonic flow. Results of the model are compatible with Tanaka’s recent extensive molecular dynamics simulations, which were originally interpreted as corroborating the spinodal theory. Implications are also consistent with spectroscopic and X-ray scattering experiments. In addition, the model has something to say about Turnbull’s relation for estimating interfacial free energies and their temperature dependence. Strengths and weaknesses of the approach presented are discussed, as is the question of whether the interpretation is distinct from the spinodal interpretation. What is different from the original spinodal interpretation is that the phase below the apparent instability temperature is still liquid, not solid. The present paper does not purport to have established an accurate account of the molecular behavior responsible for water’s anomalies. Its aim is to call attention to attractive features of the two-state model that deserve further consideration.

## Introduction

In research at the University of Michigan it has been found to be possible to supercool submicroscopic water droplets to temperatures as low as 200 K before they freeze<sup>1</sup> and then to measure rates of the homogeneous nucleation of ice.<sup>2</sup> In order to apply nucleation theory to the analysis of results, it is necessary to estimate such thermodynamic quantities as the enthalpy and free energy of freezing at deep supercooling. For this reason we have investigated various interpretations of the behavior of water. A large number of papers on this subject have been published during the past century,<sup>3–21</sup> the most popular of them postulating variations of the so-called two-state model,<sup>1,3–6,12,13,17,18,20</sup> continuum models,<sup>4,10,12,16,20</sup> and models<sup>7–9,11,14,19</sup> invoking a spinodal instability of the liquid at a temperature  $T_s$  believed to be about 227 K. The latter hypothesis has been widely discussed in recent years, and a treatment of the nucleation of ice has been explicitly based upon it.<sup>12</sup> In addition, a very recent computer simulation by Tanaka<sup>19</sup> has been considered to corroborate the existence of the spinodal.<sup>23</sup>

However plausible the spinodal theory may be, it offers nothing of utility to the interpretation of our own experimental results. This is because our liquid droplets of water attain temperatures far below the postulated temperature of absolute instability of liquid water, and the spinodal theory provides no suggestion of how to estimate the thermal properties of water

in whatever form it may exist below  $T_s$ . A possible way to extrapolate thermodynamic data to temperatures below  $T_s$  while accounting for water’s anomalies was suggested by the recent work of Vadamuthu *et al.*<sup>17,18</sup> to explain water’s density maximum at 4 °C and compressibility minimum at about 50 °C by apportioning water into high- and low-density components (known as “states” in the two-state model). The proportions of the components depended upon temperature and pressure in such a way as to reproduce the experimental data. Although Vadamuthu *et al.* did not pursue the following line of reasoning, an equilibrium constant for the transformation of one component to the other could be calculated if the mole fractions of the components were assumed to be proportional to the activities of components in the mixture. It turned out that the slope of  $\ln K$  vs  $1/T$  inferred from Vadamuthu’s apportionment suggested an enthalpy difference of the magnitude needed to explain the known thermal anomaly. Such an approach is the essence of the two-state model, a model with a long and troubled history that received such severe criticism several decades ago that it is generally considered to be untenable. Nevertheless, it was attempted to apply such model to the substantial body of data accumulated since the unfavorable verdict was reached, including the apparent divergences of several thermodynamic properties at about 227 K. The striking aspect of the Vadamuthu decomposition<sup>17</sup> that stimulated the renewed attack was the implied discontinuity in slope of the density at 225.3 K as the high-density component disappeared rather abruptly as water cooled. In the context of the two-state model this led to a

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divergence of the heat capacity of the sort needed without the requirement that the liquid freeze. The phase remaining below  $T_s$  was simply the low-density liquid component. This possible interpretation made it compelling to analyze further implications of this point of view. Additional encouragement was provided by the knowledge that a variant of the two-state model by Speedy<sup>13</sup> avoided the worst problems of prior treatments.

As mentioned above, there was no rational way to treat our experimental nucleation data in the absence of a treatment that recognized the existence of liquid water below 227 K. For example, the published ice nucleation theory<sup>22</sup> based on the spinodal at  $T_s$  made the nucleation rate diverge at  $T_s$ , even for submicroscopic droplets. If this proved to correspond to reality, there would be no way for us to interpret our experiments and we would have to conclude that water confined to such small dimensions as our droplets is not representative of natural water. We shall comment on this possibility later.

In the following the details of the present treatment will be outlined and the results will be presented in graphical form. In addition, properties previously considered to support the spinodal theory will be examined from the standpoint of the two-state model.

## Treatment

**Preliminary Remarks.** For the present purposes we shall outline a model that is obviously too simple to describe in detail what occurs as molecules of supercooled water continuously reorganize. Despite our ignorance of the exact structural changes in water as it cools, it is widely accepted that the decrease in density on cooling below 4 °C is the consequence of the increased numbers of molecules incorporated into tetrahedrally connected networks. It is possible, then, that the following model may capture enough of the essence of the effect of volumetric changes associated with the building of such a network to permit a reasonable extrapolation of thermodynamic data to deep supercooling.

It is assumed that a dynamic equilibrium

$$nM = TN \quad (1)$$

exists between  $n$  monomers  $M$  and clusters  $TN$  consisting of a characteristically bulky tetrahedral network. For example,  $TN$  might represent the pentagon rings discussed by Speedy<sup>13</sup> or, in the conventional two-state model with  $n = 1$ , simply the monomer in a different "state". We shall refer to the species  $M$  and  $TN$  as components, using the term loosely for convenience in discussion. The equilibrium constant associated with the above reaction can be expressed in standard notation as

$$\begin{aligned} K &= a_{TN}/(a_M)^n \\ &\equiv \gamma_{TN}x_{TN}/(\gamma_Mx_M)^n \\ &\equiv x/\gamma(1-x)^n \end{aligned} \quad (2)$$

where  $x$  is the mole fraction of the  $TN$  component, and  $\gamma$  a composite activity coefficient

$$\gamma = \gamma_M^n/\gamma_{TN} \quad (3)$$

can absorb the nonideality of mixing of the two components. Presumably  $\gamma$  deviates most markedly from unity at low temperatures where  $x$  gets large. We shall refer to the approximation of  $K$ , neglecting  $\gamma$ , as  $K_x$ .

The central idea of the two-state model is the assumption that water's unusual properties are consequences of such an

equilibrium. This can be seen at once, qualitatively, from the le Chatelier principle. If the equilibrium constant for the reaction were known as a function of temperature and pressure, it would be possible to derive many of the thermodynamic properties of water. Among them would be the anomalous quantities such as the coefficient of thermal expansion, heat capacity, and compressibility, all of which appear to diverge as water is progressively supercooled. In two-state treatments it is commonly attempted to derive mole fractions of the two components by a plausible apportionment of the volume, and we shall follow this practice. Of the very accurate measurements of water's density in the literature, we have selected Kell's as expressed by his polynomial fit.<sup>24</sup> From the ratio of the temperature-dependent mole fractions resulting from an initial guess of parameters is constructed  $K_x$ , a first approximation to the equilibrium constant. Because the apportionment of volumes can be carried out arbitrarily in an unlimited number of ways, we have imposed the following criteria for acceptability. The functions selected to represent the temperature-dependent volumes of the two postulated components are adjusted until (a) the van't Hoff plot of  $\ln K$  vs  $1/T$  gives as straight a line as possible over as large a range of temperature as possible without invoking activity coefficients and, (b) at the same time, the enthalpy calculated from the van't Hoff slope accounts for the heat capacity and the reaction volume change accounts for the compressibility.

Whatever else eventuates from the above approach, the coefficient of thermal expansion is guaranteed to agree exactly with the experimental data used. There is a great deal of latitude in choosing component volumes that satisfy only criterion a, and different choices imply a fair range of reaction enthalpies and volume changes. Some of these choices may also satisfy part of criterion b, but the satisfaction of one part excludes the satisfaction of the other for all but a limited range of  $n$ . Our arbitrary gauge of acceptability of a result, then, is that water's distinctive thermodynamic properties be reproduced convincingly without requiring an essential role for the activity coefficient until low temperatures are reached. As will be seen, even though the model in its conventional form ( $n = 1$ ) fails to give satisfactory results, thereby confirming the severe criticisms of the two-state model published 2 decades ago,<sup>5,25</sup> the model is agreeably successful over a physically plausible range of  $n$ . It is this aspect that was insufficiently investigated in the prior analyses that resulted in rejection of the two-state model. A detailed outline of the thermodynamic relations encountered in the treatment follows.

**Governing Relations for Two-State Model.** The volume and enthalpy per mole of the species present in the two-component solution can be expressed as

$$\bar{V}(T,P) = (1-x)\bar{V}_M(T,P) + x\bar{V}_{TN}(T,P) \quad (4)$$

and

$$\bar{H}(T,P) = (1-x)\bar{H}_M(T,P) + x\bar{H}_{TN}(T,P) \quad (5)$$

where the  $\bar{V}_i$  and  $\bar{H}_i$  are the partial molar quantities for the species  $i$ . Because there are  $[1 + (n-1)x]$  moles of water for every mole of the mixture of  $M$  and  $TN$ , eqs 4 and 5 must be divided by this amount to obtain  $\bar{V}_w$  and  $\bar{H}_w$ , the volume and enthalpy per mole of water. It is intuitively simpler to envisage the tetrahedral network in terms of partial molar volumes and enthalpies based on the moles of water contained, or

$$\bar{V}_{TNm} \equiv \bar{V}_{TN}/n \quad (6)$$

and

$$\bar{H}_{\text{TNm}} \equiv \bar{H}_{\text{TN}}/n \quad (7)$$

It follows that the volume and enthalpy changes per mole of reaction are

$$\Delta_n V = n(\bar{V}_{\text{TNm}} - \bar{V}_{\text{M}}) \quad (8)$$

and

$$\Delta_n H = n(\bar{H}_{\text{TNm}} - \bar{H}_{\text{M}}) \quad (9)$$

Following Speedy's conventions for dividing the volumes and enthalpies into normal (monomeric) and anomalous (starred) contributions, we write

$$\bar{V}_{\text{W}} = \bar{V}_{\text{M}} + \bar{V}^* \quad (10)$$

and

$$\bar{H}_{\text{W}} = \bar{H}_{\text{M}} + \bar{H}^* \quad (11)$$

so that the coefficient of thermal expansion, heat capacity, and compressibility can be similarly apportioned, or

$$\alpha = \frac{1}{\bar{V}_{\text{W}}} \left( \frac{\partial \bar{V}_{\text{W}}}{\partial T} \right)_p = \alpha_{\text{M}} + \alpha^* \quad (12)$$

$$C_p = (\partial \bar{H}_{\text{W}} / \partial T)_p = C_p^{\text{M}} + C_p^* \quad (13)$$

and

$$\kappa = \frac{-1}{\bar{V}_{\text{W}}} \left( \frac{\partial \bar{V}_{\text{W}}}{\partial P} \right)_T = \kappa_{\text{M}} + \kappa^* \quad (14)$$

Then, if the mole fraction  $x$  can be extracted from experimental data, the volume and enthalpy changes for the reaction can be estimated from the equilibrium constant via

$$(\partial \ln K / \partial T)_p = \Delta_n H / (RT^2) \quad (15a)$$

$$= \frac{1 + (n-1)x}{x(1-x)} \left( \frac{\partial x}{\partial T} \right)_p - \left( \frac{\partial \ln \gamma}{\partial T} \right)_p \quad (15b)$$

and

$$(\partial \ln K / \partial P)_T = -\Delta_n V / (RT) \quad (16a)$$

$$= \frac{1 + (n-1)x}{x(1-x)} \left( \frac{\partial x}{\partial P} \right)_T - \left( \frac{\partial \ln \gamma}{\partial P} \right)_T \quad (16b)$$

whence

$$\left( \frac{\partial x}{\partial T} \right)_p = \frac{x(1-x)}{1 + (n-1)x} \left[ \frac{\Delta_n H}{RT^2} + \left( \frac{\partial \ln \gamma}{\partial T} \right)_p \right] \quad (17)$$

and

$$\left( \frac{\partial x}{\partial P} \right)_T = \frac{x(1-x)}{1 + (n-1)x} \left[ \frac{-\Delta_n V}{RT} + \left( \frac{\partial \ln \gamma}{\partial P} \right)_T \right] \quad (18)$$

according to the two-state model. From eqs 4–18 it follows

that

$$\begin{aligned} \bar{V}_{\text{W}} \alpha^* &= \left( \frac{\partial \bar{V}^*}{\partial T} \right)_p \\ &= \frac{\Delta_n V}{[1 + (n-1)x]^2} \left( \frac{\partial x}{\partial T} \right)_p + \frac{x}{1 + (n-1)x} \left( \frac{\partial \Delta_n V}{\partial T} \right)_p \end{aligned} \quad (19a)$$

$$\begin{aligned} &= \frac{x(1-x)\Delta_n V}{[1 + (n-1)x]^3} \left[ \frac{\Delta_n H}{RT^2} + \left( \frac{\partial \ln \gamma}{\partial T} \right)_p \right] + \\ &\quad \frac{x}{1 + (n-1)x} \left( \frac{\partial \Delta_n V}{\partial T} \right)_p \end{aligned} \quad (19b)$$

$$\begin{aligned} C_p^* &= (\partial \bar{H}^* / \partial T)_p \\ &= \frac{\Delta_n H}{[1 + (n-1)x]^2} \left( \frac{\partial x}{\partial T} \right)_p + \frac{x}{1 + (n-1)x} \left( \frac{\partial \Delta_n H}{\partial T} \right)_p \end{aligned} \quad (20a)$$

$$\begin{aligned} &= \frac{x(1-x)\Delta_n H}{[1 + (n-1)x]^3} \left[ \frac{\Delta_n H}{RT^2} + \left( \frac{\partial \ln \gamma}{\partial T} \right)_p \right] + \\ &\quad \frac{x}{1 + (n-1)x} \left( \frac{\partial \Delta_n H}{\partial T} \right)_p \end{aligned} \quad (20b)$$

and

$$\begin{aligned} \bar{V}_{\text{W}} \kappa^* &= -(\partial \bar{V}^* / \partial P)_T \\ &= \frac{-\Delta_n V}{[1 + (n-1)x]^2} \left( \frac{\partial x}{\partial P} \right)_T - \frac{x}{1 + (n-1)x} \left( \frac{\partial \Delta_n V}{\partial P} \right)_T \end{aligned} \quad (21a)$$

$$\begin{aligned} &= \frac{-x(1-x)\Delta_n V}{[1 + (n-1)x]^3} \left[ \frac{-\Delta_n V}{RT} + \left( \frac{\partial \ln \gamma}{\partial P} \right)_T \right] - \\ &\quad \frac{x}{1 + (n-1)x} \left( \frac{\partial \Delta_n V}{\partial P} \right)_T \end{aligned} \quad (21b)$$

Results corresponding to the conventional two-state treatment are recovered from eqs 19b, 20b, and 21b if  $\Delta_n H$ ,  $\Delta_n V$ , and  $\gamma$  are assumed to be constant and  $n$  is taken to be unity. Alternatively, if  $\Delta_n H$ ,  $\Delta_n V$ , and  $\gamma$  are treated as constants and  $n$  is assumed to be 5, in the limit of small mole fraction  $x$  the results are identical to those derived by Speedy<sup>13</sup> from considerations of statistical fluctuations in the formation of bulky pentagon rings.

Note that, if  $x(T)$  and  $K(T)$  are known  $\alpha^*(T)$  and  $C_p^*(T)$  can be calculated directly from eqs 19a and 20a, without reference to the activity coefficient  $\gamma$ . How to devise plausible estimates of  $x(T)$  and  $K(T)$  from Kell's experimental density data and how to infer the magnitude of  $n$  were sketched at the beginning of the section. A more detailed account is given in the next section.

**Inference of Parameters.** The fitting of experimental data by a two-state model is far from unique. Even after arbitrarily choosing  $n$ , the number of water molecules in the postulated tetrahedrally coordinated aggregates, an infinite number of alternative mole fractions  $x(T, P)$  of the TN species can be constructed to satisfy the relations 19b, 20b, and 21b if the collective activity coefficient  $\gamma(T, P)$  is adjusted to compensate. What would lend credence to the exercise of fitting parameters to the model would be to find a solution with physically reasonable parameters that yields a satisfactory representation of the experimental determinations of  $\alpha(T)$ ,  $C_p(T)$ , and  $\kappa(T)$

without having to invoke a severe departure of  $\gamma$  from constancy until a high concentration of TN is reached at low temperatures. It is easiest to take the model seriously if it accounts for both the density maximum and the compressibility minimum without even requiring  $\gamma$  to deviate from unity. It is the last criterion that governed the choice of parameters adopted for the model.

To begin the process, we investigated two representations of the temperature dependence in an attempt to obtain plots of  $\ln K_x(T)$  with substantially different van't Hoff enthalpy values. It was assumed that the molar volumes of the high- and low-density components are either choice "A"

$$\bar{V}_i = V_i^0 \{1 + \alpha_i[(T - T_1) + b(c + (T - T_1)^2)^{1/2}] - (P - P^0)\kappa_i^0[1 + \sum_{s=1}^N \beta_{is}(T - T_m)^s]\} \quad (22a)$$

or choice "B"

$$\bar{V}_i = V_i^0 \{1 + \sum_{r=1}^N \alpha_{ir}(T - T_m)^r - (P - P^0)\kappa_i^0 \times [1 + \sum_{s=1}^N \beta_{is}(T - T_m)^s]\} \quad (22b)$$

where  $i$  stands for M or TNm,  $T_m$ , for the melting point, and  $T_1$  for an adjustable parameter. Because the reasons for selecting the two forms are trivial, the forms are presented here solely for documentation of the results to be reported. Over the range of interest of 200–400 K, little is gained by carrying out terms beyond cubic in eq 22. Rough estimates of  $\alpha_{ir}/\alpha_{i1}$  and  $\beta_{is}/\beta_{i1}$  for initial guesses can be based on results for normal liquids. Presumably,  $V_M^0$  and  $V_{TNm}^0$  correspond, respectively, to densities somewhat greater and appreciably lower than 1 g/cm<sup>3</sup>. From the initial guess of the parameters of eq 22 are derived preliminary representations of  $\bar{V}_M(T)$ ,  $\bar{V}_{TNm}(T)$ , and  $\Delta_n V(T)$ , leading to an initial estimate of  $x(T)$ , via eqs 4 and 6, of

$$x(T) = (\bar{V}_{\text{expt}} - \bar{V}_M)/[n\bar{V}_{TNm} - (n-1)\bar{V}_{\text{expt}} - \bar{V}_m] \quad (23)$$

where Kell's polynomial fit of his experimental density was adopted to represent  $\bar{V}_{\text{expt}}$ . The fit was extrapolated to 228 K, well inside the stated range of validity, to get some idea of the behavior of  $x$  as the temperature of the hypothetical instability is approached. Vedamuthu *et al.* suggest that the representation is satisfactory down to at least –30 °C. The foregoing procedure yields a preliminary estimation of  $K_x(T)$  vs  $1/T$ . Plots of  $\ln K_x(T)$  vs  $1/T$ , of  $C_p(T)$ , and of  $\kappa(T)$  were viewed continuously as parameters in eq 22 and in  $\Delta H_n(T)$  were varied. Parameters  $\Delta_n H^0$  and  $\Delta_n C_p$  in

$$\Delta_n H(T) = \Delta_n H^0 + \Delta_n C_p(T - T_0) \quad (24)$$

were also adjusted to make a reference curve  $\ln K_{\text{ref}}(T)$  pass through  $\ln K_x(T)$ , where

$$\ln K_{\text{ref}}(T) = \ln K(T_m) + \int_{T_m}^T \frac{\Delta_n H(T)}{RT^2} dT \quad (25)$$

For the purposes of the present study it was found to be unnecessary to go beyond the linear term in eq 24, and  $T_0$  was taken to be 273.15 K for choice A and 227 K for choice B. The function  $x(T)$  implies  $(\partial x/\partial T)_p$  which, in turn, provides an evaluation of  $(\partial \ln \gamma/\partial T)_p$  via eq 17. This function was integrated numerically to yield the factor  $\gamma(T)$  needed to correct

$K_x(T)$  to  $K(T)$  of eq 1 in order to check the numerical consistency of the manipulations. Results were satisfactory.

During the course of the above refinements of parameters, the anomalous and normal contributions to the heat capacity were calculated, the former contribution from eq 20a and the latter from

$$C_p^M(T) = \sum_{k=0}^4 c_k(T - T_m)^k \quad (26)$$

The anomalous and normal contributions to the compressibility are expressed in eqs 21 and 22. Note that the quantities  $\Delta_n V$  for eq 21 are already available from the fits of  $\alpha(T)$ ,  $K(T)$ , and  $C_p(T)$ . In eq 22 it is reasonable to expect the compressibility coefficients  $\beta_{is}$  of the less dense component to be somewhat larger than those of the more compact component, and this is reflected in the parameters determined by Vedamuthu *et al.*<sup>18</sup> Because the closeness of fit of the various calculated functions with the experimental data could be monitored conveniently as the parameters for  $\bar{V}_M(T)$ ,  $\bar{V}_{TNm}(T)$ ,  $\Delta_n H(T)$ ,  $C_p^M(T)$ , and  $\kappa(T)$  were adjusted, refinements converged quickly to compromises incorporating the aforementioned criteria for acceptance. That the compromises were less contrived and led to more convincing results for some values of  $n$  than for others provided an estimate of the size of the TN aggregates compatible with the present model.

In the refinements it was possible to view progress continuously, graphically and analytically, as the parameters were adjusted to improve the agreement between calculated and observed quantities. Such convenient procedures for analyzing the two-state model were not available 2 decades ago when it was concluded that the model was untenable.

Recall that the method of determining  $x(T)$ , the mole fraction of the TN species, ensures that the fit of  $V_{\text{expt}}(T)$ , and hence of  $\alpha(T)$ , is both smooth and exact by its definition (eq 23), although this definition by its nature implies as large a contribution from the activity coefficient as is necessary to make the fit exact. To reiterate, our basis for narrowing the choices in the construction of  $x(T)$  is the ability to reproduce  $\alpha(T)$ ,  $C_p(T)$ , and  $\kappa(T)$  satisfactorily without invoking severe departures of  $\gamma$  from constancy until low temperatures are reached. In particular, the maximum in the density at 4 °C and the minimum in the compressibility at ~50 °C should arise naturally without having to rely on the derivatives  $(\partial \ln \gamma/\partial T)_p$  and  $(\partial \ln \gamma/\partial P)_T$ . Without such a limitation, an unlimited range of parameters would be able to reproduce all of the thermodynamic data by the expedient of adjusting the activity coefficient. The degree to which the two-state model is successful when the activity coefficient is restricted by our criteria is illustrated in the next section.

## Results

Some systematic implications about the size of the tetrahedral aggregates can be deduced at once from the forms of eqs 8 and 19–21. Since the refined values of  $\bar{V}_M(T)$  and  $\bar{V}_{TNm}(T)$  do not depend strongly upon  $n$ ,  $\Delta_n V$  increases approximately linearly with  $n$ , whereas  $\Delta_n H(T)$  varies much more modestly. This has the effect of making  $\kappa^*(T)$  increase and  $C_p^*(T)$  fall as  $n$  is increased and thereby leads to an estimate of the optimum range of  $n$  for the model.

We shall first focus on the cases of  $n = 1$  and  $n = 5$ . The former had been the choice in most (but not all) of the earlier applications of the two-state model, and the latter was suggested by Speedy on physical grounds. To illustrate some of the consequences of selecting different parameters for apportioning the volume, we chose two quite different starting points for the

**TABLE 1: Parameters Used To Represent Water in Eqs 22a and 24<sup>a</sup>**

components	$\Delta_1 H^0$	$\Delta_1 C_p$	$V_i^0$	$\alpha$	$b$	$c$	$T_1$	$\kappa_i^0$	$\beta_{i1}$
both	-8.23	9			0.694	484	259		
low density			1.088	0.0004				35.5	0.004
high density			0.8	0.001				24.8	0.0025

<sup>a</sup> Energy in kJ/mol, temperature in K, volume in cm<sup>3</sup>/g, compressibility in 10<sup>6</sup> × bar<sup>-1</sup>.

**TABLE 2: Parameters Used To Represent Water in Eqs 22b and 24<sup>a</sup>**

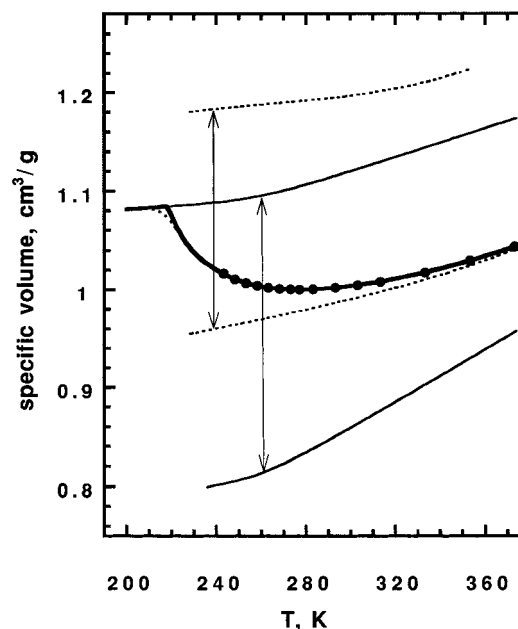
components	$\Delta_5 H^0$	$\Delta_5 C_p$	$V_i^0$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\kappa_i^0$	$\beta_{i1}$	$\beta_{i2}$
both	-15 800	6.8							
low density			1.19	0.000 17	$5.0 \times 10^{-7}$	$2.2 \times 10^{-8}$	36	0.0026	$2.9 \times 10^{-5}$
high density			0.9757	0.000 51	$8.7 \times 10^{-7}$	$5.8 \times 10^{-9}$	32.5	0.0022	$2.9 \times 10^{-5}$

<sup>a</sup> Energy in J/mol, temperature in K, volume in cm<sup>3</sup>/g, compressibility in 10<sup>6</sup> × bar<sup>-1</sup>. Parameters for other  $n$  values, choice B, are similar.

case of  $n = 1$ . For one of the choices (choice A, based on eq 22a) the specific volume of the bulky species was assumed to be approximately that of ice, and for the other (choice B, based on eq 22b), the volume of the TN species was adjusted to make  $\Delta_1 V$  (the volume increase per mole of water transforming in the reaction of eq 1) approximately that inferred by Speedy from structural considerations. For choice B the TN volume, then, was substantially larger than that of ice. This choice was also made for the case of  $n = 5$ . When the reference volume of the denser component and the coefficients of thermal expansion of both components were adjusted in an attempt to satisfy the aforementioned criteria, very different results were obtained for the A and B choices. An even wider range of initial volumes could be made to generate defined "equilibrium constants"  $K_x(T)$  that exhibited well-behaved van't Hoff plots, provided that the coefficients of thermal expansion were adjusted suitably. This shows how unrestrictive the criterion for acceptability based on the van't Hoff plot is, taken by itself. We were unable, however, to find a solution with  $n = 1$  that satisfied that criterion while also fitting the heat capacity and compressibility.

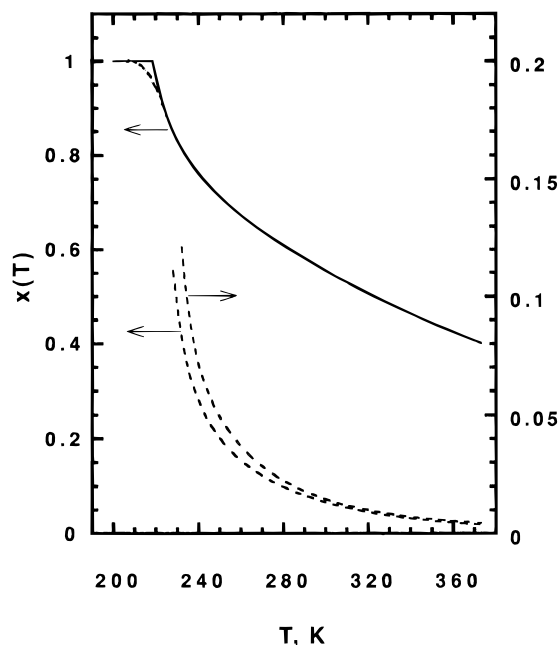
Choice A led to an apparent equilibrium constant with a van't Hoff slope corresponding to  $\Delta_1 H \approx 8$  kJ/mol, and choice B yielded a slope nearly twice as large. Since a small value of  $n$  tends to make both  $C_p^*$  and the  $C_p^*/\kappa^*$  ratio large, choice A came closest to fitting  $C_p^*(T)$  while utterly failing to fit  $\kappa(T)$ , and the reverse was true for choice B. Compromise fitting parameters for the results presented in the figures are listed in Tables 1 and 2.

In terms of the  $x(T)$  values implied, the results differ from those of Vedomuthu *et al.*<sup>17</sup> with choice A giving a somewhat larger mole fraction of the bulky component and choice B a substantially smaller mole fraction. Since the Vedomuthu approach was not designed with the present thermodynamic correlations in mind, however, the published  $x(T,P)$  function does not satisfy eq 18 very well, and a larger deviation of  $\gamma$  from unity would be required to satisfy eq 15. Our results for the A and B choices are presented graphically. Figure 1 illustrates how the specific volume of warm water falls as water cools then rises until, according to the model, the postulated dense component is depleted. Below that temperature, liquid water behaves more or less normally again but exists in the low-density form. The heavy solid curve is extrapolated abruptly to  $x = 1$  (illustrated for choice A) in much the same way as done by Vedomuthu *et al.*, and a short (dashed) segment contiguous with the curve carries out the extrapolation less abruptly in a manner that might be more reasonable physically. There was no intention of Vedomuthu *et al.* to attach a physical meaning to the  $x = 1$  intercept occurring in the experimentally unexplored region, but in view of the fact that the intercept turns out to be close to the proposed spinodal temperature,  $T_s$ , the intercept is of some interest to consider. In Figure 2 are plotted

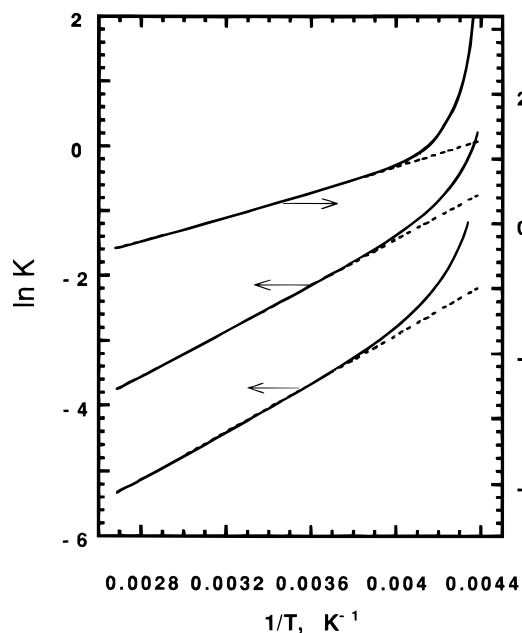


**Figure 1.** Specific volumes for water and for several choices of its postulated components: (points) experiment, ref 24; (light lines for high- and low-density components) choice "A" (solid) and choice "B" (dashed); (heavy solid line) fit of experiment extrapolated abruptly to the pure low-density component as in ref 17; (short-dashed segment) one choice of a smoother extrapolation. A large degree of arbitrariness in fitting is evident, but only for a limited range do the fits yield model solutions reproducing the other thermodynamic quantities. On the scale of the plot, the curves corresponding to  $n = 1$  and  $n = 5$  for choice B are indistinguishable.

three representations of  $x(T)$ , the mole fraction of the bulkier species. Two represent the A and B choices for  $n = 1$  and the other is for  $n = 5$ , choice B. In Figure 3 are plotted the temperature variations of the functions  $\ln K_x$  and the associated reference curves  $\ln K_{\text{ref}}$  corresponding to the three  $x(T)$  curves of Figure 2. These show the extent of the linear regions of the van't Hoff plots, the regions not requiring temperature-dependent activity coefficients. A constancy of  $\gamma$  through the region including 4 °C means that water's density maximum can be reproduced exactly without calling upon activity coefficients. In the top curve of Figure 4 is a comparison of the experimental and model (choice A) heat capacities, suggesting that the model gives a reasonable representation of reality while, at the same time, exhibiting the marked anomaly heretofore attributed to a spinodal instability. The more gentle solid curve, although still manifesting a strong anomaly, shows the effect on  $C_p$  of smoothing the  $x(T)$  function near the  $x = 1$  intercept. Both solid curves are based on eq 20a and thereby implicitly incorporate the collective activity coefficient. If the classical two-state model is used, however (by taking  $\gamma$  to be unity in eq



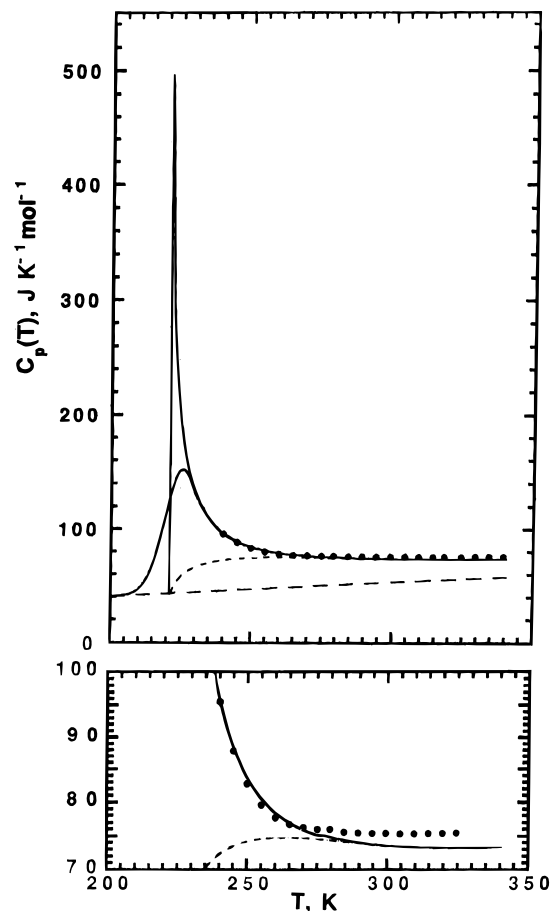
**Figure 2.** Mole fraction  $x(T)$  of bulky component from apportionments of the volume illustrated in Figure 1: (solid curve) choice A,  $n = 1$ ; (dashed curves) choice B. Left-hand scale is for  $n = 1$ , and right-hand scale is for  $n = 5$ .



**Figure 3.** Van't Hoff plots for equilibrium constants calculated from mole fractions of Figure 2. Solid curves represent  $\ln K_s(T)$ , and dashed curves represent extrapolations from  $\ln K_s(T_m)$  to  $\ln K_{ref}(T)$  via eq 25. Curves from top to bottom are for choice A,  $n = 1$ , choice B,  $n = 1$ , and choice B,  $n = 5$ .

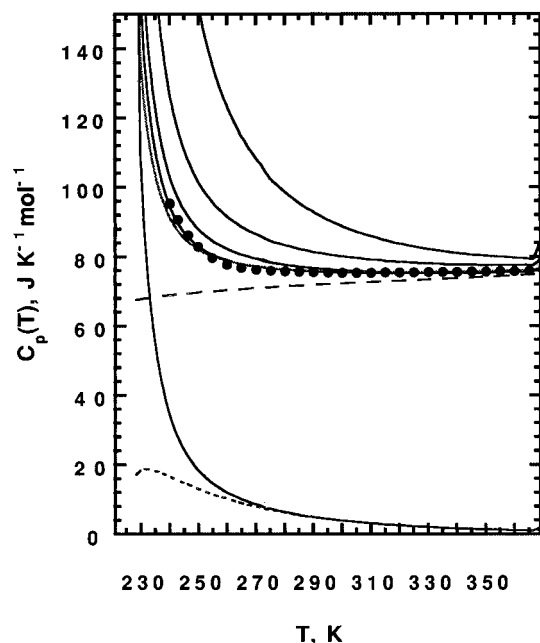
20b), the result is the unconvincing curve of short dashes. For all of the curves, the line of long dashes represents the normal component of the heat capacity about which more will be said subsequently. Casting the results in a less favorable light is the lower plot of Figure 4, which reveals that, in order to fit the upsweep of the anomalous heat capacity in the mean, the model curve with its insufficient curvature undershoots the heat capacity at higher temperatures. As mentioned earlier, the failure of the  $n = 1$  model is even more severe in its representation of the compressibility.

Next we illustrate results obtained when we incorporate the estimate of the volume excess of the bulky species chosen by



**Figure 4.** Comparison of experimental heat capacities (points, from ref 9) with those calculated by the model, choice A,  $n = 1$ . Top frame shows divergent  $C_p(T)$  calculated from abrupt extrapolation illustrated in Figures 1 and 2 and more moderate  $C_p(T)$  calculated from the smoother extrapolation, with both curves from eqs 20a and 26. Dotted curve shows eq 20b, taking  $\gamma$  to be unity. The “normal” component of  $C_p(T)$  is represented by long dashes. Bottom frame shows an enlarged section showing the poor fit at higher temperatures forced by the compromise to fit experimental results in the mean in the anomalous region. This compromise also leads to a “normal” component appreciably lower than inferred from experiment (refs 6 and 26).

Speedy in his two-state fluctuation treatment, guided by structural considerations in tetrahedral binding. For  $n = 1$  this corresponds to our choice B but for all other  $n$  values from 2 to at least 8, apparently acceptable van't Hoff plots can be obtained with very nearly the same excess  $[\bar{V}_{TNM}(T) - \bar{V}_M(T)]$ .<sup>13</sup> This uniformity allows a systematic investigation of the effect of  $n$  in model calculations. Increasing  $n$  has the effect of reducing the mole fraction of the bulky species derived from the  $\bar{V}_{expt}(T)$  data, as shown in Figure 2, although the mass fraction is not much changed. It also reduces  $C_p^*$  while increasing the anomalous compressibility. What is more important is the better form of the calculated heat capacity reflected in Figure 5 for  $n$  in the vicinity of 5 and, as expected from Speedy's work, the enormously better representation of the compressibility manifested in Figure 6 for the same magnitude of  $n$ . As shown in the latter plot for this choice of  $[\bar{V}_{TNM}(T) - \bar{V}_M(T)]$ , the minimum in the compressibility curve is reproduced naturally without requiring any contribution from the collective activity coefficient. On the other hand, the analogous curve for  $n = 1$  for choice A shows no vestige of the minimum and the full burden of forcing an agreement with experimental results would fall upon the activity coefficient. Even the derived “normal” contribution to the heat capacity discriminates between the two model choices, since  $C_p^M(T)$  agrees well with the normal



**Figure 5.** Comparison of experimental heat capacities (points, ref 9) with those based on choice B with a range of sizes of the bulky species. The curves in the order of decreasing  $C_p(T)$  are for values of 1, 3, 5, 6, and 8 for  $n$ . The dashed line underlying the solid curves is the corresponding normal component of the model. At the bottom of the figure are representations of the anomalous component calculated via eq 20a (solid curve) and 20b assuming  $\gamma = 1$  (dashed). Only above the freezing point are the two in approximate agreement.

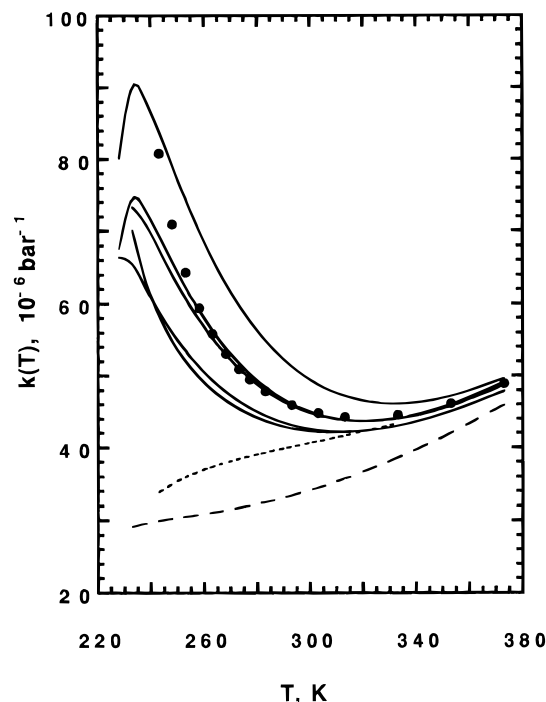
component deduced experimentally by Angell and co-workers<sup>6,26</sup> for choice B, but the  $C_p^M(T)$  for choice A falls well below Angell's result.

To investigate whether even more satisfactory solutions of the model exist, computations were run with other values of  $n$ , and their results are shown in Figures 5 and 6. It was found that values of  $n$  smaller than 5 and larger than 6 yield poorer compromises in their ability to fit both the heat capacity and compressibility. All values, of course, fit the coefficient of thermal expansion exactly by definition.

## Discussion

**Inference of Size of the Bulky Species.** Results of applying the two-state model in its modifications with  $n$  ranging from 1 to 8 have been sketched in the foregoing text. The value of unity for  $n$  had been selected because it was the variant conventionally applied in the past and because it seemed, at first, to supply the thermodynamic extrapolation needed for deeply supercooled water. As we have seen, however, the results turned out to be unsatisfactory in several aspects. On the other hand, the variants with  $n$  in the vicinity of 5 were quite successful when coupled with Speedy's excess volume.<sup>13</sup> If there is any physical validity to the model, it is unlikely that the reaction of eq 1, between  $n$  monomers and an  $n$ -mer, conveys the true physical picture for such a complex fluid as water when restricted to a single  $n$  value of, say, exactly 5. It is even less convincing to imagine that a value of unity for  $n$  makes any physical sense when it is recognized that the interatomic distances most heavily implicated in the formation and dissipation of the bulky "state" are not even those between neighboring molecules but between *next-nearest* neighbors.<sup>17,27</sup>

Speedy<sup>13</sup> had already identified pentagon rings as logical candidates for the bulky species. Moreover, molecular dynamics simulations by Mausbach, Schnitker, and Geiger<sup>14</sup> corroborated Speedy's prediction of the magnitude of  $\chi(T)$ , the temperature-



**Figure 6.** Comparison of experimental compressibilities (points, refs 9 and 18) with those calculated by the model over a range of sizes of the bulky species. The solid curves in the order of decreasing  $\kappa(T)$  at 250 K are for values of 8, 6, 5, 3, and 1 for  $n$ , choice B. The dotted curve is for  $n = 1$ , choice A. Underlying the curves for the total compressibility is a dashed curve illustrating the model's normal component of the compressibility.

dependent concentration of pentagon rings. In addition, the simulations found that hexagon rings proliferated in parallel with the pentagons as water cooled and with similar concentrations. The present results are pleasingly, perhaps fortuitously, in agreement with the molecular dynamics picture of water's properties.

For the case of  $n = 1$ , choice A, the specific volume of the low-density component, was of the general magnitude as that for ice and, therefore, not inconsistent with the known way for water molecules to pack together. Less intuitive is the rather high specific volume of the bulky component for choice B plotted in Figure 1, since it is much higher than that of any form of ice. It is, however, comparable with the volume occupied by a segment of clathrate structures. To find the consequences of adopting a more icelike volume for the bulky component while retaining the choice B volume for the dense component, we made additional runs. In the quality of fitting experimental data the results were comparable to those for the Speedy excess volume but the optimum agreement with thermodynamic measurements occurred in the vicinity of  $n = 12$ , not 5 or 6. Therefore, the so-called two-state model is consistent with a broad distribution of TN species in which the initial aggregates formed upon supercooling are likely to be small with large specific volumes while the ones at deeper supercooling may well include some larger, more icelike aggregates. Indeed, according to nucleation theory, at deep supercooling this is inevitable in the stochastic process of the formation and dissolution of precritical embryos. These embryos could be larger than a half-dozen molecules but still be too small to act as critical nuclei for freezing. Nucleation theory is insufficiently developed to give a reliable value for the size of critical nuclei, but the classical theory suggests that critical nuclei at 200 K contain about 60 molecules.<sup>2</sup> Critical nuclei are even larger at lower degrees of supercooling. Therefore, the distribution of sizes of the TN species in the two-state model

does not appear to be in danger of precipitating a catastrophic growth of ice. Also, it should be pointed out that the formation of precritical nuclei cannot, in itself, be responsible for water's anomalies because such nuclei are naturally formed in perfectly normal liquids.

**Kauzmann's Paradox.** A further aspect of the model results needs to be considered. Of particular interest are results in the vicinity of 200 K, the temperature to which our own droplets are cooled in supersonic expansions. Does the anomalously high heat capacity, which leads to a rapidly falling entropy as the liquid cools, imply a state in which the supercooled liquid has a lower entropy than ice at the same temperature? That is, according to the model, does the manifestation of Kauzmann's paradox<sup>28</sup> arise in highly supercooled water? If so, it would undermine the model. Before this question is answered, it is instructive to consider the model heat capacities based on the "abrupt" and the "smoothed"  $n = 1$  extrapolations of  $x(T)$  plotted in Figure 4. Although the two results look strikingly different, with the "abrupt" curve diverging more or less in the manner proposed by advocates of the spinodal theory, the two  $C_p(T)$  curves do not of course imply any difference between the heat needed to warm supercooled water from 200 K to the freezing point. Experimental values for the heat and entropy of fusion for water at the freezing point are 6.003 kJ mol<sup>-1</sup> and 22.0 J K<sup>-1</sup> mol<sup>-1</sup>.<sup>29</sup> For both the abrupt and smoothed extrapolations the heat of fusion at 200 K is 1.9 kJ mol<sup>-1</sup>, exhibiting a fairly large but not troublesome decrease from the value at the freezing point. The entropy drop depends somewhat upon the mode of smoothing. For the smoothed  $C_p(T)$  of Figure 4,  $\Delta S_{\text{fus}}$  is 5.0 J K<sup>-1</sup> mol<sup>-1</sup>. If the disappearance of the high-density component had been extrapolated along a curve much more gradual than the smooth curves of Figures 1 and 2, the loss of enthalpy and entropy at 200 K would have been less.

For the case of  $n = 6$ , if the depletion of the high-density component is assumed to be abrupt at  $T_s$ , the above curve-fits to the data yield a value for the heat and entropy of fusion just below  $T_s$  of 2.14 kJ mol<sup>-1</sup> and 5.7 J K<sup>-1</sup> mol<sup>-1</sup>. At 200 K, the values fall to 1.4 kJ mol<sup>-1</sup> and 2.2 J K<sup>-1</sup> mol<sup>-1</sup>, lower than for the  $n = 1$  case in significant measure because the "normal" contribution to  $C_p$  for  $n = 1$  had to be adjusted to an unreasonably low value to achieve a compromise fit of  $C_p$  above  $T_s$ . It will be pointed out presently that the thermal anomaly responsible for the great drop in the entropy of fusion is significantly moderated in the small droplets cooled to 200 K in supersonic jets.

Although the entropy of fusion at 200 K has fallen considerably from its value at the freezing point according to the model, no problem was encountered with Kauzmann's paradox.<sup>28</sup> On the other hand, in a recent treatment of ice nucleation proposed by Pruppacher,<sup>22</sup> the spinodal theory was invoked, and the anomalous heat capacity at the critical point  $T_s$  was assumed to be so divergent that the heat of fusion went to zero at  $T_s$ . It is simple to show that Kauzmann's paradox is "violated" before  $T_s$  is reached under these circumstances.

It is worthwhile to compare the free energy of fusion at 200 K derived from the present model with that estimated from the heat capacity guessed by Huang and Bartell,<sup>2</sup> whose droplets cooled to 200 K before freezing. The present  $n = 5$  model yields 0.96 kJ mol<sup>-1</sup>, a value 0.1 kJ mol<sup>-1</sup> smaller than that of the prior estimate.

**Some Weaknesses of Model.** The principal results of the present formulation of the two-state model have already been outlined. Although they show that with suitable choices of parameters the model is quite able to reproduce water's thermodynamic anomalies including the divergences that gave

birth to the spinodal hypothesis, that fact alone does not prove the model's correctness. Before continuation of the discussion of the results, it is fair to point out certain weaknesses in the present implementation of the model. We should also inquire why a two-state model should be seriously considered at this time after its underpinnings were subjected to searching scrutiny 2 decades ago when the model was essentially discarded as untenable.<sup>5,25</sup> The most obvious weaknesses in the present treatment are the following.

(a) The inference of the relative proportions of the two components by apportioning the volume between them is not unique. Apportionment was subjective, guided by the aforementioned criteria to achieve an equilibrium constant requiring as modest a deviation of activity coefficients from constancy as possible while reproducing  $C_p(T)$  and  $\kappa(T)$ . Apportionments meeting the stated criteria could be constructed from a range of component volumes, with different initial guesses implying appreciably different sizes of the bulky species. If the excess volume  $\Delta_n V/n$  were known, *ab initio*, the arbitrariness of the model would be greatly diminished. Although Speedy has made very plausible estimates of this excess from known clathrate structures, it will take more accurate computations than can be carried out currently to establish water's structure and density, especially at extreme supercooling, to test the model's validity.

(b) It is not obvious that such a complex mixture should behave as ideally as proposed. Still, it is fair to mention that Kauzmann<sup>5</sup> also used unit activity coefficients in his critical analysis of the two-state model—and came to a conclusion very different from ours.

(c) Although the "anomalous" contributions to the thermodynamic quantities were reasonably established by the model assumptions, the "normal" contributions were adjusted arbitrarily, governed by no criterion other than to make the total quantities agree with experimental results as well as possible.

(d) Our analyses extrapolated Kell's curve-fit of the volume of water well below the intended range of application. Although this no doubt led to quantitative errors, it probably did not distort results qualitatively.

(e) Little consideration was given to the possibility that the size of the TN aggregates may increase systematically as the temperature falls. For example, Stillinger<sup>8</sup> has suggested that progressive supercooling may "produce cluster sizes that diverge as  $T_s$  is approached from above". However, such a catastrophic increase in the density fluctuations as would accompany such an agglomeration does not seem to have been observed in X-ray scattering experiments.<sup>30</sup> Nevertheless, the principal points in Stillinger's 1980 discussion of the consequences of the tetrahedral networks ring true today.

In view of the above arbitrariness it is by no means ensured that the present treatment has any objective validity. This being the case, our justification of the treatment is that it does broaden perspectives about water's properties and in a very simple way and also suggests a way to extrapolate thermal data to deep supercooling. Our main aim has been to demonstrate that the model has features that are too attractive to be ignored. Alternative interpretations are considered in the next section.

**Alternative Points of View.** Although it is beyond the scope of this paper to present a critical review of arguments against the two-state model, it is reasonable to mention a few of the more germane. Why did Kauzmann reject the two-component model despite his own "habit" of "thinking about [water and aqueous systems] in such terms?"<sup>5</sup> What he did was to make plausible guesses about the enthalpy and volume differences between the two components without carrying out the detailed analyses performed here. Today's computer methods *enor-*



mously facilitated the present decompositions. On the basis of his not unreasonable guesses, Kauzmann showed that it was difficult to account for the temperature variation of the heat capacity and the temperature and pressure dependence of the coefficients of thermal expansion and compressibility. In the current analysis our approach was from a somewhat different direction. We began by accepting as input data the known anomalous coefficient of thermal expansion<sup>24</sup> and derived the enthalpy difference and compressibility consistent with it. Moreover, we explicitly incorporated into the equilibrium constant the quantity  $n$ , the number of monomers forming the bulky aggregates. Kauzmann included  $n$  in the enthalpy and volume changes per mole of water but not in the equilibrium constant. Whether by accident or by having captured elements of the truth, our results turned out to account for the anomalously sharp rises of  $C_p^*$  and  $\kappa^*$  at deep supercooling. This information was not fully known to Kauzmann in 1975.

Shortly after Kauzmann's analysis was published, Endo<sup>25</sup> presented other reasons why two-state models "are inapplicable to liquid water". To do this, he used parameters derived by Davis and Litovitz.<sup>31</sup> It turns out that the simplifying assumptions in fitting led to two-state parameters that are far from general for a two-state approach and are very different from ours. These parameters were incorporated into equations involving a small difference between large, uncertain quantities. This is the source of at least part of the inconsistency encountered by Endo. On the other hand, Endo's earlier two-state model treatment of relaxation times (an observable not examined in the present paper) had been successful.<sup>32</sup>

Recently, Tanaka<sup>19</sup> presented the results of extensive molecular dynamics computations that contributed significant insights into the behavior of highly supercooled water. These simulations were interpreted as supporting the spinodal theory.<sup>19,23</sup> The question is whether the results provide any evidence against the two-state model. Tanaka's calculated change in density with temperature showed a marked break in slope at about 213 K (close to  $T_s$  on the temperature scale of the TIP4P model potential). Note that such a break is characteristic of the present model also, as can be seen in the heavy curve of Figure 1. Interpreted in terms of the spinodal theory, it was unexpected and rather bizarre to find in the molecular dynamics results that the proposed instability limit separated two distinct *liquid* phases, not a liquid from a solid. By contrast, in the two-state model the system is naturally liquid on both sides of the "break".

Tanaka also found that the low-temperature O—O pair correlation functions at  $T \leq 213$  K differed substantially from those at temperatures at and above 233 K, leading him to infer that two distinct phases were involved. If we add perhaps 12 °C to Tanaka's temperatures to convert from the TIP4P to experimental temperatures, we see that Tanaka's division into two regions, one characterized by a low-temperature structure and one by a high-temperature structure, corresponds well to the  $n = 5$  results in Figure 2. The region between 225 and 245 K separates the nearly pure TN species from the fairly pure monomer. Again, there is no contradiction.

An important effect highlighted by the temperature dependence of Tanaka's pair correlations is the increase in population of next-nearest O—O neighbors at distances of about 4.5 Å (characteristic of the tetrahedrally coordinated species) and the decrease of the 3.4 Å populations as the concentration of the bulky form grows. This increase, which is exactly what would be expected from the present model, has also been observed in X-ray diffraction studies of water,<sup>27</sup> and its significance has been stressed often by Robinson and his co-workers.<sup>17,18,20</sup>

In discussing his simulations, Tanaka argued in favor of the

spinodal hypothesis on several grounds. First, he maintained that "there must exist a critical point at about 213 K [temperature scale of the TIP4P potential]—because of the large density fluctuation [encountered] at 213 K". Of course, the anomalous compressibility itself, which is well accounted for by the two-state model, implies a large density fluctuation according to statistical thermodynamics.<sup>33</sup> Tanaka then stated that because of the sharp drop in potential energy on cooling, "water must undergo a kind of transition in order to preclude [the] Kauzmann paradox". But, as shown above, the present two-state model<sup>10</sup> suffers no such trouble, even though the enthalpy does experience a marked drop. The same avoidance of Kauzmann's paradox cannot be claimed for Pruppacher's spinodal treatment of supercooling and nucleation.<sup>22</sup>

As pointed out by Tanaka, fluctuations in density can be large when a system is approaching a critical point. Evidence that the latter type of instability is not being approached as supercooling deepens has been reported by Xie *et al.*<sup>30</sup> These workers observed no onset of density fluctuations in low-angle X-ray scattering experiments that could be attributed to the increasing correlation lengths to be expected for a critical point. The authors claimed, instead, that their measured density fluctuations were associated "with an increasing fraction of water molecules participating in clusters". Such an interpretation is the essence of the present model.

Recall that the motivation of the present treatment was to find a way to analyze the results of our water droplets at temperatures well below  $T_s$ , the proposed instability temperature. Our "droplets" contain an order of  $10^4$  or fewer molecules. Robinson, whose research on water stimulated the present treatment in the first place, has suggested that water, confined to small dimensions, may not be "real water".<sup>34</sup> For example, water in very fine capillaries has a density different from that of bulk water.<sup>17,35</sup> It is possible, then, that the reason our submicroscopic drops of water did not experience the critical point postulated by proponents of the spinodal point of view is that they are too small and too short-lived. Here, it is of interest that one of the formulators of the spinodal theory has accepted the results of Tanaka's molecular dynamics (MD) simulations in support of that theory.<sup>17,35</sup> Tanaka's sample, consisting of only 216 molecules, was considerably smaller than our droplets, and his time of observation was 3 orders of magnitude briefer than ours. Still, because of the periodic boundary conditions imposed in the MD runs, Tanaka's system was denied a surface, and surface effects lie at the heart of Robinson's misgivings about water in confined spaces. Moreover, after all of the above discussion of the possible effects of anomalies on droplets cooled to 200 K, surface effects may play a key role in the fate of the droplets we observe. The Laplace pressure imposed on their interior by surface tension is quite large, on the order of 600 atm. At such high pressures water's anomalies are severely washed out,<sup>9</sup> as can be seen from the thermodynamic identity

$$(\partial C_p / \partial P)_T = -T(\partial^2 V / \partial T^2)_P \quad (27)$$

Since the present model accepts  $V(T)$  as input data, its implications for  $(\partial C_p / \partial P)_T$  are necessarily correct. According to Kell's analytical representation<sup>24</sup> of  $V(T)$ , the rate at which  $C_p$  changes with pressure is, in J/mol per 100 atm,  $-57$  at 230 K,  $-19$  at 235 K, and  $-9$  at 240 K.

**Spectroscopic Studies.** In addition to the thermodynamic, X-ray scattering, and computer studies of water's anomalies, there have been many spectroscopic investigations. A definitive discussion of spectral changes has been given by Angell and Rodgers.<sup>12</sup> The presence of isosbestic points in spectra taken over a series of temperatures suggests that fairly well-defined

bulky aggregates are formed at the expense of a denser structure as water is cooled. Almost all of the analyses of the effects of temperature on intensities of the hypothesized two forms of water have implicitly been based on the two-state model with  $n = 1$ . Results have consistently found enthalpy differences of the general magnitude inferred in the present work for the  $n = 1$  case. If the presumed equilibrium had been interpreted in terms of higher values of  $n$ , appreciably different enthalpy differences would have been derived from the van't Hoff slopes.

**Implications about Interfacial Free Energies.** One other aspect of supercooled water deserves comment. A useful empirical relation suggested by Turnbull<sup>36</sup> makes the interfacial free energy  $\sigma_{sl}$  for the liquid–solid boundary proportional to the heat of fusion. From this relation it is possible to estimate  $\sigma_{sl}$  from  $\Delta H_{fus}$  and thereby to predict various properties such as the temperature dependence of the rate of nucleation of crystals from a melt. For many substances the heat of fusion does not vary greatly with temperature so that there is little ambiguity in applying Turnbull's relation. For water, on the other hand, the difference between the heat capacities of the liquid and solid is so great that  $\Delta H_{fus}$  drops rapidly as the temperature falls. Some workers assume that  $\sigma_{sl}$  remains proportional to  $\Delta H_{fus}(T)$ , falling steadily with it.<sup>37</sup> If such a proportionality did hold, it would imply, for example, that  $\sigma_{sl}$  would be far lower at 200 than at 240 K. But the results of the supersonic nucleation studies indicate that the interfacial free energy is not very different at 200 K than at 240 K.<sup>2</sup> Because this contradicts the proportionality postulate, it has cast doubt on the supersonic results. Now, it is entirely reasonable to expect, as the liquid and solid phases become more and more alike as implied by a smaller and smaller enthalpy difference, that the interfacial free energy must fall accordingly. But water is an anomalous liquid. If the present two-state model is correct, a natural explanation of the similarity between the 200 and 240 K interfacial free energies can be made while accepting the idea that both the interfacial free energy and heat of fusion fall as the liquid and solid become more similar to each other. If water is a mixture of the two components, clearly the low-density constituent resembles ice much more closely than does the high-density constituent. Hence, it will adsorb preferentially at the interface and occupy a disproportionate fraction of the interfacial area even at 240 K. Therefore, the Gibbs adsorption isotherm relating interfacial free energies to adsorption suggests, in the case of water, that  $\sigma_{sl}$  probably drops quickly from its value at the freezing point to an approximately asymptotic value by 240 K. In this way the intuitive argument can be seen not to contradict the experimental results.

**Is the Model Distinct from the Spinodal Model?** A conspicuous feature of the temperature dependence of  $x(T)$ , the concentration of the bulky species derived in the foregoing treatments, is the speed with which it increases at deep supercooling. This acceleration is much faster than would be expected for a nearly ideal mixture [with unit activity coefficients and an approximately constant  $\Delta_n H(T)$ ]. The implied higher escaping tendency of the denser component, or special "attraction" of the bulky aggregates for each other, is consistent with many prior discussions dealing with water's anomalies. Several points of view have been expressed to explain its origin. Stillinger's arguments<sup>8</sup> discussed in the foregoing attributed this "clumping tendency" to an energetic advantage. Stanley and Teixeira<sup>38</sup> showed that, quite apart from possible energetic advantages, there is a topological element in such a tendency. Speedy and Angell<sup>7</sup> argued that the source of the anomalies may "lie in volume cooperativity rather than in enthalpy cooperativity". Irrespective of the cause of the sharp rise in  $\gamma$

seen in the results of the present model, the upsurge is not inconsistent with the existence of an instability at deep supercooling. In its present form, however, the model does not require that the phase below the instability be solid, as discussions prior to Tanaka's computational results assumed it to be.

## Concluding Remarks

Whatever the detailed molecular behavior may be as water cools, the conclusion seems inescapable that bulky molecular aggregates of some kind must be forming in order to explain the liquid's unusual properties. Results of the two-state model as described in the foregoing suggest that pentamers and hexamers tend to be favored in the aggregation process, although the possibility of larger, less bulky aggregates coming into play at some stage, is not precluded. Even though the formulation of the model is that for two "states", the results suggest a bridge to a continuum model. Although the model has by no means been proven to be a faithful representation of the aggregation, its consequences are consistent with a large body of information about the fluid. When the adequacy of the model is weighed, it should be recognized that no attempt has been made in this initial inquiry to derive the fitting parameters optimally or with precision. Such an undertaking would be justified only after demonstrating the general viability of the approach, and the viability was left in considerable doubt after the negative findings of previous analyses. It turns out that the model offers many attractive features including simplicity and a plausible means of extrapolating thermodynamic data. Its main support is Ockham's razor, for it would seem to provide the least complicated scheme to account for water's anomalies.

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