

values found for tetradecylammonium chloride (2.03)³⁷ and for octadecyltrimethylammonium bromide (2.0-2.4)⁴².

Discussion of the k^+ Values. The association rate constants k^+ (see Table IV) are in the range expected for diffusion-controlled association reactions. k^+ decreases as the chain length increases as in the case of sodium alkylsulfates^{35,43} or sulfonates,⁴³ alkylpyridinium chlorides⁴⁴ or bromides,^{43,44} and alkylammonium chlorides.³⁷ Note that the values of k^+ given in ref 43 are much lower than those given in the other references due to the fact that for the former authors the slope of the τ^{-1} vs. a plot gives k^+ whereas in Aniansson and Wall's theory it gives k^+/n . The k^+ values found for $\text{Me}(\text{C}_6)_2$ and $\text{Me}(\text{C}_7)_2$ are slightly smaller than those found at 25 °C for octylammonium chloride⁴⁵ ($2.8 \times 10^9 \text{ s}^{-1}$), dodecylammonium iodide³⁷ ($3.1 \times 10^9 \text{ s}^{-1}$), and tetradecylammonium chloride³⁷ ($2.5 \times 10^9 \text{ s}^{-1}$). This difference might be due to the fact that the dialkyl surfactants need more space at the surface of the micelle to penetrate into it, or that a larger electrostatic repulsion exists as the dialkyl surfactants approach the micelle resulting from a higher ionization of the dialkyl micelles compared to the ionization of monoalkyl micelles.⁴¹ The same explanations have been proposed by Hoffmann⁴⁶ to account for the lower value of k^+ found for another surfactant bearing two alkyl chains, the sodium *p*-6-dodecylbenzenesulfonate, compared to the k^+ value found for straight-chain surfactants.

Discussion of the ΔV Values. It is well known, from density measurements principally, that the formation of ionic micelles is usually accompanied by a positive volume change. Therefore positive values of ΔV are given in Table V, although only absolute values can be determined by ultrasonic absorption measurements. We are not aware of volume change data obtained by density measurements for dialkylammonium surfactants. However, a comparison between our results and the results of the literature can

be made by considering the volume change by alkyl chains. The mean values of this volume change, calculated from the values given in Table V, are 3.8 and 4.7 cm^3/mol for $\text{Me}(\text{C}_6)_2$ and $\text{Me}(\text{C}_7)_2$, respectively. Extrapolation of these values gives 5.5 cm^3/mol for a surfactant with eight carbon atoms per alkyl chain. This value is in good agreement with those found at 25 °C by density for monoalkyl surfactants. It is between 3.8 cm^3/mol , the ΔV value found for octylammonium bromide,⁴⁷ and 8.1 cm^3/mol , the ΔV value found for trimethyloctylammonium bromide.⁴⁸ It appears from these results that the volume change increases as the number of CH_3 groups on the nitrogen head group increases.

Conclusion

The kinetic results of the dialkylmethylammonium chloride surfactants of relatively short chain length investigated in the present study do not show drastic changes compared to the result obtained for monoalkyl surfactants. Perhaps the most striking result is that the relaxation times and the dissociation rate constants are close to those found for monoalkyl surfactants of about the same alkyl chain length. The cmc's are in agreement with previous studies on dialkyldimethylammonium chlorides. The aggregation number determined by ^{13}C NMR for dihexylmethylammonium chloride is in agreement with the results obtained for monoalkylammonium surfactants. The kinetic study of dialkylammonium surfactants of longer chain length would perhaps show larger differences but should be carried out by other techniques. Shock-tube methods, for instance, could be used to look for relaxation processes in aqueous solution of dialkylammonium surfactants of at least nine carbon atoms per alkyl chain.

Acknowledgment. The author is grateful to Elisabeth Krempf (NMR Central Facilities, Université Louis Pasteur, Strasbourg, France) for excellent technical assistance in running the ^{13}C NMR spectra and Dr. Jacques Simon (Centre de Recherches sur les Macromolécules, Strasbourg, France) for indicating the method of preparation of diheptylmethylammonium chloride.

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Heat Capacity of Water at Extremes of Supercooling and Superheating

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Low-temperature heat capacities for water and D_2O have been remeasured with sample preparation and data analysis procedures different from those used in the original studies of this anomalous region. Self-consistent results have been obtained with reproducibilities of 1%. Comparisons are made with the behavior in the superheated region at 1-atm pressure calculated from a refined equation of state by Haar et al. It appears that the kinetic metastability limit of the liquid (nucleation terminated) at both hot and cold extremes may be reached at the same value of the liquid heat capacity.

In 1972 Rasmussen et al.¹ reported that the heat capacity of water increases very rapidly on supercooling below ~ -15

°C and reaches values of $\sim 1.5 \text{ cal g}^{-1} \text{ deg}^{-1}$ ($113 \text{ J mol}^{-1} \text{ deg}^{-1}$) at -38 °C, at which temperature crystallization of

ice I terminated the measurements. At the other extreme, equally striking increases in heat capacity of water near the superheating limit have been determined by extrapolations to low pressure (based on corresponding states arguments) of high-pressure stable-range data.^{2,3} It had earlier been suggested by Anisimov et al.⁴ that water would show causally related anomalies in C_v at high- and low-temperature extremes.

The purpose of this report is to present new and improved data for the low-temperature range and to point out that the phase change that terminates the metastable region at each extreme occurs in the region of sharply increasing heat capacity at about the same value.

There is a particular need for improved data at low temperatures. The results of Rasmussen et al.,¹ which have helped generate much of the current interest in supercooled water, were essentially of exploratory character. They revealed an interesting phenomenon but exhibited differences of up to 10% between data sets from different methods of measurement and different instruments. Nevertheless, for want of better, these data have been used as a basis for predicting and analyzing the behavior of other properties such as sound velocities,^{5,6} possibly to the detriment of comparisons with experiment. For instance, if the values of C_p used were to contain an error of +5% growing in between -25 and -33 °C in the region of fast-increasing C_p , then a predicted velocity minimum based on

$$v = \left(\frac{1}{\rho \kappa_s} \right)^{1/2} = \left(\frac{C_p}{C_v} \frac{1}{\rho \kappa_T} \right)^{1/2} \quad (1)$$

would disappear, if C_v were assumed constant. If C_v were (more correctly) subjected to the same correction, then the predicted velocity minimum and the associated K_s maximum would be displaced to lower temperature, and a phenomenological relationship to the maximum in C_v ,^{7,8} which would now be revealed more clearly at ~ -20 °C, would become more obvious. Likewise, the thermodynamic absurdity

$$0 > C_p/C_v = [1 - T\alpha^2/\rho C_p \kappa_T]^{-1} \quad (2)$$

obtained⁶ by boldly extrapolating to $T < -40$ °C power-law equations fitting α , C_p , and κ_T data measured at higher temperatures, will not appear.

We have therefore carefully repeated the low-temperature measurements a number of times by using differential scanning calorimetry of dispersed droplet samples, prepared and measured by different investigators using different sample preparation techniques and somewhat different data analysis methods. We present here sets of emulsion data that are self-consistent to $\pm 1\%$ and agree

to 0.5% with bulk sample data on the low-temperature limit of the latter, -13 °C. At the low-temperature extreme, the new data differ by almost 5% from the average values previously reported.

Experimental Section

In the low-temperature emulsion measurements, the water contribution to the total heat capacity of the two-phase sample has been separated not only by the technique of comparing frozen and unfrozen sample data used previously¹ but also by the technique of offsetting the non-aqueous component with an equal mass of dispersant-surfactant solution in the reference pan. Comparison of results with literature data in the temperature range above 0 °C suggests that these techniques are of approximately the same overall reliability. The former suffers from the addition of the random errors from two scans, while the latter suffers from a combination of errors from two weighings of small quantities and additional uncertainties from possible changes in emulsion-volume fraction of water during transfer to the sample pan.

Measurements were performed with the Perkin-Elmer DSC-2 instrument equipped with the Perkin-Elmer Scanning Auto Zero accessory. Samples of mass ≈ 15 mg were down-scanned from ~ 20 °C at 10 deg min^{-1} on a sensitivity setting of $2 \geq \text{mcal/s}$. In the case of investigator I's determinations, the pen displacement with the instrument in the isothermal hold condition was carefully checked, for both empty and loaded pans, at short intervals between the initial and final temperatures of the scanning run. Under favorable instrument conditions this is unnecessary. However, in practice, variations in these relative isothermal hold pen displacements, which would imply heat capacity errors of up to 5% for small samples studied in uncalibrated wide-temperature range scans, can at times be observed, and this practice is necessary to obtain the best performance from the instrument.⁹

The question of whether the lowest temperature C_p results are influenced by partial crystallization during cooling cannot be satisfactorily answered by the obvious procedure of making measurements during temperature increase rather than decrease, though data above -33 °C were confirmed by this method in earlier work.^{1c} The reason is that any measurements must start from an "isothermal hold" position, and a modest time, hence temperature, interval (~ 2 °C) must be allowed for the instrument-sample ensemble to reach its correct steady-state condition for measurement. The isothermal hold temperature cannot be set too close to T_H because the total elapsed time near T_H determines the probability of nucleation. Thus the temperature is already above the region, $T < 35$ °C, in which the threat of incipient crystallization influence is real, before the measurement can commence. A better confirmation of the absence of such artifacts is perhaps the absence of any precrystallization upswings in the case of emulsions of binary solutions in which the anomalous character of water has been "quenched" by the second component. The behavior of such solutions is systematically presented for the case of $\text{H}_2\text{O} + \text{H}_2\text{O}_2$ in a previous paper.⁹

The most serious source of error in these measurements at low temperature would appear to be the temperature calibration. This must be assumed the same for downscans as it is for upscans because, due to supercooling of standards, calibrations are always conducted on upscans. Some liquid crystal standards, in which transition

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TABLE I: Heat Capacity of Water in $\text{J K}^{-1} \text{mol}^{-1}$

T/K	T/°C	emulsion samples ^a			bulk sample		emulsion sample ^b n-octane	suggested value
		n-octane	methylcyclohexane carrier	av	this work ^e	lit. data		
290	17	75.4			75.4	75.4 ^c		
285	12	75.4			75.2	75.5 ^c		
280	7	75.5			75.5	75.6 ^c , 75.5 ^d		
275	2	75.4			75.5	75.9 ^d		
270	-3	76.2	75.9	76.0	75.7	76.2 ^d		76.1
265	-8	76.6	75.7	76.2	76.6	76.8 ^d	76.4	76.4
260	-13	77.5	77.3	77.4	77.6		76.9	77.6
255	-18	78.3	79.5	78.9			78.7	78.8
250	-23	80.6	82.2	81.4			81.4	81.4
245	-28	84.4	86.4	85.4			84.5	85.2
242	-31						88.4	
240	-33	92.7	92.7	92.7			91.4	92.3
239	-34						94.4	
238	-35	96.6	96.8	96.7			96.1	96.5
237	-36						98.7	99.0
236	-37						102.2	102.7

^a Investigator I, sample freeze technique. ^b Investigator II, reference offset techniques. ^c Handbook of Physics and Chemistry, CRC press, 58th Edition. ^d Anisimov et al., ref 15. ^e Investigator I.

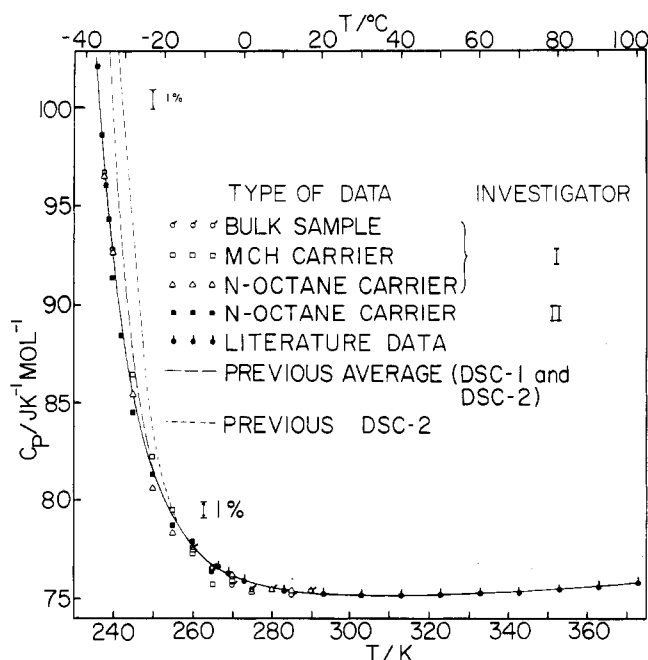


Figure 1. Heat capacity of water in normal and supercooled temperature ranges at 1-atm pressure. (●) Literature data for bulk sample. (○, □, △) Data obtained in this study by investigator I for bulk sample (○) and emulsion samples by using MCH (□) and *n*-octane carriers (△); (■) data obtained in this study by investigator II for emulsion sample in an *n*-octane carrier.

strengths are small, but supercooling does not occur, are very desirable.

Results

The new data for water are collected in Table I and displayed graphically in Figure 1. Discussion of the form of this heat capacity function and of the manner in which it is affected by changes of external pressure and additions of second components is given elsewhere.⁹⁻¹¹

A redetermination of C_p for D_2O has reproduced earlier reported DSC data¹ to better than the experimental uncertainty of $\pm 2\%$. The new data for bulk and emulsion

TABLE II: Heat Capacity of D_2O in $\text{J K}^{-1} \text{mol}^{-1}$

T/K	T/°C	bulk ^a		lit. data	emulsion ^a		emulsion ^b
		run I	run II		run I	run II	
298.15	25			84.3 ^c			
295				82.75 ^e			
290	17	83.6		82.4 ^d			
289	16			83.58 ^e			
285	12	83.75			85.4	83.5	
284	11			83.62 ^e			
280	7	84.1	84.9		84.9	83.7	
279	6			84.36 ^e			
275	2	84.7	85.2		85.1	84.1	
270	-3	86.1	86.0		86.0	85.0	84
265	-8	87.4	87.2		87.2	86.5	85.8
263	-10						87.7
260	-13				89.6	88.7	
255	-18				93.3	92.3	92.1
253	-20						95.5
250	-23				99.9	99.2	101.3
245	-28				109.3	109.5	110.0
242	-31				119.6		
240	-33				129.3		129.2

^a Investigator I. ^b Reference 1. ^c Termichieskie Konstanty Westchestv (Thermal Constants of Substances) Academy of Sciences, USSR Moscow, 1965, Part I, p 33. ^d NBS Circular 500. ^e Long, E. A.; Kemp, J. D. *J. Am. Chem. Soc.* 1936, 58, 1829.

samples are compared with the old and with literature data for bulk samples in Table II.

Discussion

Anomalous increases in liquid heat capacity at low temperature of the form of Figure 1 are not found in other molecular liquids, even those with otherwise water-like properties such as H_2O_2 and N_2H_4 , nor in mixtures of water with more than 20% of these liquids (even though some of these mixtures can be studied during continuous cooling down to -140°C where they vitrify).⁹

On the other hand, all molecular liquids that are internally stable against decomposition must exhibit anomalies of this character on sufficient superheating. This follows from the general form of the fluid equation of state, which shows that a region of mechanical instability must exist in the isobaric V - T diagram for all pressures below the critical pressure. Such mechanical instabilities are generally illustrated by reference to the impossible negative-compressibility region in the ordinary van der Waals

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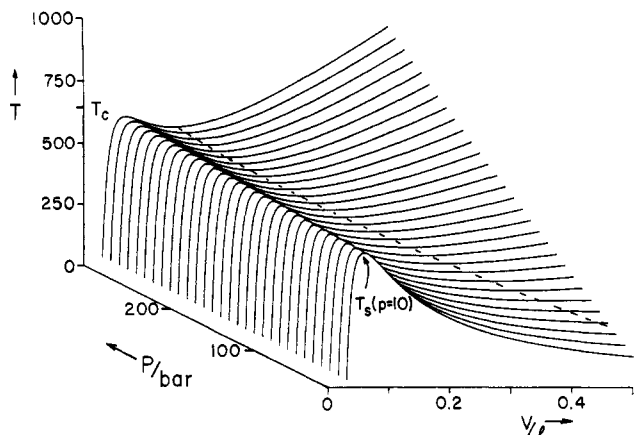


Figure 2. Isobars for water at subcritical pressures according to the van der Waals equation showing the metastability limits at various pressures.

equation P - V isotherm for $T < T_c$. For qualitative purposes, we illustrate the corresponding T - V behavior in Figure 2 for a series of isobars at $P < P_c$ calculated for water by using a van der Waals equation with parameters obtained, as usual, from the T_c and P_c values. The maxima correspond to minima in the corresponding P - V isotherms and hence to points at which the superheated liquid becomes mechanically unstable and must spontaneously rupture. Of course, the simple van der Waals equation is inadequate to describe fluid water in detail, and it is therefore not surprising that the T - V maximum and hence the superheating limit of 277 °C predicted by this equation for 1-atm pressure is less than the experimental superheating limit, T_H , of 279.5 °C, observed for small droplets by different authors,^{12,13} or 302 °C obtained by Skripov and co-workers from explosive boiling nucleation rate studies.¹⁴ The latter value is close to that calculated by Apfel for nucleation in bulk.¹² The theoretical limit (the spinodal temperature T_s) should actually lie somewhat above the homogeneous nucleation temperature (which is the kinetically limited reflection of the impending catastrophe) and has been estimated at 305 °C by Eberhard and Schnyders¹⁵ from equation of state calculations and at 324 °C at 1 atm by Skripov.¹⁴ In this region the impending instability must be anticipated by large fluctuations in density and entropy, and these will be reflected in the magnitudes of the related thermodynamic properties, compressibility and heat capacity, in which we are interested here.

Although direct measurements of heat capacity or expansivity in this region have not yet been made they may be calculated with the equation of state described by Haar et al.¹⁶ The compressibility calculations up to 240 °C from the same equation are in very good agreement with values obtained recently by Hareng and Leblond¹⁷ by combining direct light-scattering measurements of adiabatic compressibility with extrapolated density data. Values of C_p calculated by Haar¹⁸ at normal pressure are plotted in

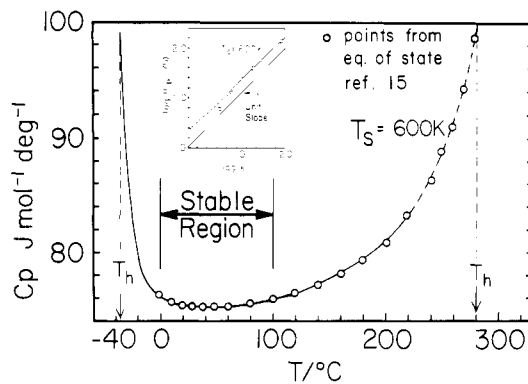


Figure 3. Combination of low-temperature-range data of this study with metastable superheated range data calculated from the equation of state of Haar et al. for the superheated range. The metastable state low- and high-temperature limits observed for small droplets are -42 and 280 °C, respectively (marked T_h). Inset: Test of critical type law for high-temperature equation of state C_p values after subtracting a constant "background" of 75 cal mol⁻¹ deg⁻¹. The plot uses $T_s = 600.0$ K and yields a slope of unity as indicated by the solid line in the inset. Use of (calculated) C_p values beyond the C_p range of those measured in low-temperature experiments yields slightly lower T_s ($T_s \rightarrow 596$ K) and smaller slopes ($\gamma \rightarrow 0.4$).

Figure 3 together with the low-temperature data. It is notable that even the upswing in C_p at low temperatures is predicted by this equation. The increases at high temperature are more gradual than those predicted from a scaling equation suggested by Lienhard.^{2,3}

The compressibility data of Hareng and Leblond,¹⁷ which were in good agreement with earlier data to 180 °C of Trinh and Apfel⁵ and more recent data to 240 °C of Skripov and co-workers,¹⁴ were shown to fit very well an equation of the familiar critical law form

$$\kappa_T = A(1 - T/T_s)^{-\gamma} \quad (3)$$

with $T_s = 588$ K and $\gamma = 1$. This form had also been tested by one of the present authors³ on calculated heat capacities based on Lienhard's equation, under the impression that a value of $\gamma = 1$ was predicted by mean field theory. However, it now seems that $\gamma = 1$ is only applicable at the critical density. Away from the critical density, i.e., approaching a spinodal point, it appears from theoretical analyses by Compagner¹⁹ and Speedy²⁰ that the exponent should be $1/2$ for κ_T and also for α and C_p .

If we take the calculated C_p values of Haar covering the same C_p range as has been measured at low temperatures, we find that after subtracting a constant "background" contribution of 75 J K⁻¹ mol⁻¹ the excess C_p can be fitted to eq 1 with $T_s = 600.0$ K and $\gamma = 1.0$ —values similar to those found by Hareng and Leblond—as shown in the insert to Figure 3. On the other hand, extension of the equation of state calculations (into regions where no validity would be claimed by its authors) shows $C_p \rightarrow \infty$ at 595.9 K (cf. 597 K by Skripov¹⁴) and the limit is approached with a smaller eq 1 slope, $\gamma \approx 1/2$, as the new theoretical treatments suggest. It is unfortunate that, because of metastability and nucleation kinetics, it will not be possible to resolve the problem of the appropriate power law by experiment, as in the case of critical phenomena.

It has been shown elsewhere⁹ that the excess heat capacity of supercooled water obtained by subtracting from the Table I values a background C_p (determined from binary molecular and ionic solution data described else-

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where⁷⁾ is also well described by eq 3 in the form

$$C_{p,\text{excess}} = A'(T/T_s - 1)^{-\gamma} \quad (4)$$

(because now $T > T_s$) with a T_s value of 226 K and $\gamma \approx 1.0$. Interestingly enough, this singular temperature is just 5 K below the lowest freezing point ever achieved for pure water samples (cloud-chamber experiments).²¹ The implied possibility that the low-temperature phenomenon might be due to an instability was discussed in some detail in an earlier paper²² and has now been incorporated into a broad unified treatment of high-temperature, low-temperature, and negative-pressure instabilities in liquid water by Speedy.²³

For the emulsion droplets studied here, which freeze commencing at -38.5°C , $\epsilon(=T/T_s - 1)$ at the phase change is 0.038. The corresponding value for ϵ at the superheating limit of liquid-suspended droplets is 0.078 if we use $T_s = 600$ K from Haar's equation and $T_h = 553$ K from droplet-superheating limit studies.^{9,10} However, this value of T_h may be too low since it corresponds with nucleation at the silicone oil plus water surface.¹² For bulk nucleation T_h is estimated to be about 298°C (571 K) by Apfel, and explosive nucleation measured by Skripov et al.¹¹ yields $T_h = 573$ K, for which case $\epsilon = 0.045$, very close to the value at freezing. On the other hand the liquid heat capacities at the droplet superheating and supercooling limits are remarkably similar. This could be rationalized by arguing that, since C_p is proportional to the mean-square entropy fluctuations and since a critical nucleus is essentially a special entropy fluctuation, a correlation of nucleation probability and C_p might be expected.

A quantitative theory for the low-temperature heat-capacity behavior, in particular the apparent accord with a critical law, is currently lacking. Stanley and Teixeira²⁴ have recently shown that the singularity, if real, could be associated with a percolation threshold for clusters of "four-bonded" water molecules, hence amorphous icelike density fluctuations, in the liquid. On the other hand, Speedy²⁰ has now shown that all the volumetric observations on superheated, stretched (negative pressure), normal, and supercooled water can be self-consistently explained by postulating the existence of a spinodal ($\kappa_T \rightarrow \infty$) line bounding the mechanically stable liquid regime and deriving, by a Landau expansion, an equation of state that yields P_s on fitting to the available volumetric data. The form of this P_s, T_s boundary line is that of a normal liquid at high temperature, but at lower temperature and negative pressures, it departs from the normal van der Waals behavior (which is to constantly increasing negative P_s with

decreasing T_s) and at $T_s = 35^\circ\text{C}$ and $P_s = -2100$ bar, it reverses slope. The reversal point corresponds with the intersection of the spinodal with the extrapolation, to negative pressures, of the observed temperatures of density maxima.²⁰ The spinodal (instability) thus reappears at positive pressures at a temperature *below* the freezing point. The peculiar reversal would be a feature common to liquids in which the lowest energy state, which is approached with decreasing temperature, is correlated with the largest volume state. Unfortunately, there are very few such liquids (SiO_2 and some tetrahedrally coordinated antimonides and tellurides) so the phenomenon cannot be broadly studied.

Both the percolation and the spinodal models have attractive and challenging features and will doubtless stimulate increasing experimental and theoretical work in this area. However, a tendency evident in some of the current literature to see these two approaches as somehow mutually exclusive should be discouraged. The language used in ref 22 to describe the molecular nature of the increasing density fluctuations which the power law for the compressibility required to be present ("density fluctuations presumably arise and decay by the migration of large $\text{O}\cdots\text{H}-\text{O}$ angle ($\rightarrow 180^\circ$) hydrogen bonds which 'prop open' the expanded structure *when present in high local concentration* but allow collapsed dense regions to form when local concentrations are smaller") accurately previews the topological picture provided by the percolation model.²⁴ Future refinements of the current simplified percolation model to incorporate the *actual* continuous distribution of hydrogen bond energies and other interaction terms may well lead to an equation of state containing an instability at low temperatures, as indeed *is contained* in the optimized empirical equation of state of Haar and colleagues (which we have only used in this paper to discuss the *high-temperature anomalies*²⁵). In this case the two approaches would obviously be mutually reinforcing.

Both approaches are, however, antagonistic to heterophase fluctuation interpretations of water anomalies since the latter contain no reason for excluding any liquids susceptible to crystallization from showing qualitatively similar anomalies.

Acknowledgment. We are indebted to the Office of Naval Research and the National Science Foundation for support of this research under Agreement and Grant Nos. N00014-78-C-0035 and DMR 77-04318A1, respectively, to Lester Haar of the National Bureau of Standards for providing the equation of state data plotted in Figure 3, and to Robin Speedy for some very timely and helpful comments on, and corrections to, the manuscript.

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