

## Toward a Model for Liquid Water<sup>1</sup>

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*A new model is proposed for liquid water. It is obtained by consideration of the two transitions (melting and boiling) which define the liquid phase. These transitions are discussed with the aid of two analogies to well-known phenomena in polymer physical chemistry. In analogy to the helix-coil transition in polypeptides and polynucleotides, the melting of ice is viewed as a process consisting essentially of the destruction of the orderly interconnected small rings of hydrogen bonds characteristic of the crystal. The fact that the breakup of interconnected small rings is cooperative, even when unaccompanied by the breaking of bonds which are not parts of rings, is clearly seen by inspection of the theory for the putatively analogous helix-coil transition. The condensation of water vapor is viewed in analogy to gelation in reversibly polymerizing systems, an analogy which interprets its cooperativity. Taken together, these interpretations of the phase transitions indicate that the liquid can be viewed as an infinitely and randomly branched "gel" of (rapidly interchanging) hydrogen bonds in which closures of rings (primarily large rings) are present at random but in which there is no significant preference for an ordered array of small rings. These concepts also lead naturally to an interpretation of the triple point and sublimation. The random gel model is seen to be consistent with most of the known properties of liquid water. In particular, the radial distribution function, infrared and Raman spectra, dielectric properties, density maximum, and properties of the supercooled region are discussed briefly here.*

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“It must be jelly, 'cause jam don't shake like that.”  
anon.

## 1. INTRODUCTION

Theories of liquids fall into two classes: (1) effects, based solely on an assumed intermolecular potential and the principles of statistical mechanics, to predict the very existence of the liquid state as an entity separated from gaseous and crystalline states by discontinuities (first-order phase transitions) and (2) “model” theories in which at least some aspects of supramolecular liquid “structure” are assumed, on the basis of which conclusions are drawn and compared with experiment. Unquestionably, a convincing theory of type (1) is what one ultimately wants. Equally unquestionably, efforts to develop such a theory should be focused on substances simpler than water.

On the other hand, the need for a theory in the case of liquid water is very pressing, particularly for the discussion of many biophysical problems. Therefore, many type (2) theories have been presented for liquid water in the last half century or so.<sup>(1)</sup>

In the area of theories of type (2) it is essential not to forget that agreement of calculations based on any model with experimental results does not prove the validity of the model; such agreement may be fortuitous, particularly if the number of arbitrary parameters is large. Furthermore, disagreement of the theoretical conclusions with experimental results can disprove the model only if the calculations on the model are performed without further assumptions or approximations, a circumstance seldom encountered. Therefore, it is clearly important to explore, however qualitatively, every conclusion which may be drawn from a model and to effect comparison of theoretical conclusions with every relevant experimentally determined property rather than merely to achieve precise comparison of such an approximate calculation with only one or a few experimentally observed properties.

Among the experimental observations which model theories of liquid water have tended to ignore are the two phase transitions (melting and boiling) which define the liquid, the very properties which the more rigorous type (1) theories have been at such great pains to explain.<sup>4</sup> There has also been a tendency, though not a universal one, to forget the supercooled region of the liquid.

<sup>4</sup> It is important not to confuse the ability of model theories to predict the locations of these phase transitions with the ability to predict their very existence (i.e., the existence of the liquid). Once one assumes the existence of the liquid by postulating a specific model for it, one can, of course, calculate the partition function corresponding to that model and thereby obtain a curve displaying the temperature dependence of the (appropriate) free energy (at specified volume or pressure). The points where this curve crosses those for the gas and crystal (also calculated from specific models) are the calculated boiling and melting points, respectively. Unless, however, one has obtained these three free-energy curves as different solutions of the *same* general model, one cannot claim to have predicted or interpreted the phase transitions.

The present considerations represent an attempt to carve a path intermediate between the two types of theories described above. They approach the problem of the two phase transitions via analogies to two phenomena which have been widely investigated in polymer physical chemistry. Specifically these analogies relate a major feature of the helix-coil transition in polypeptides and polynucleotides to a putative corresponding feature in the melting of ice and relate the essential physics of reversible gelation in a three-dimensional polymerizing system to that of condensation of water vapor.

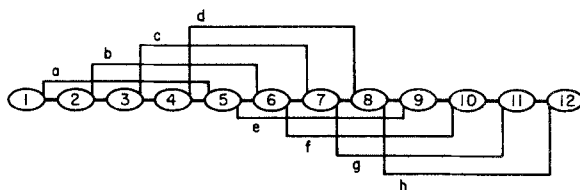
We shall consider these two phase transitions in Secs. 2 and 3, respectively, and comment on the nature of the triple-point phenomenon in Sec. 4. In Sec. 5 we show that the picture of liquid water that emerges from these considerations of the bounding phase transitions is in qualitative agreement with most of the known properties of the liquid itself, e.g., its radial distribution function, dielectric properties, infrared and Raman spectra, etc.

## 2. MELTING AND THE ANALOGY TO THE HELIX-COIL TRANSITION

Here we approach the problem of the nature of liquid water by asking how it may differ from ice. Recognizing that melting is describable as a mathematical discontinuity, we resist any temptation to view the liquid as some sort of extrapolation of the crystal (however "disordered").

A cooperative process such as a phase transition can be described crudely, though essentially correctly, as one which, though difficult to start, tends to proceed to completion under conditions adequate to start it. Thus, ice melts not at all below  $0^{\circ}\text{C}$  (at 1 atm) but melts completely upon only an infinitesimal increase of temperature at this pressure. However, a closer look at the situation reveals a basic puzzle. The cooperativity is clearly in this case somehow to be ascribed to a process of breaking hydrogen bonds (H bonds). This cooperativity causes the process to proceed catastrophically at  $0^{\circ}\text{C}$  only up to a point—a point which must be far short of the point where all H bonds are broken since the evidence for intact H bonds in liquid water is indisputable. Further catastrophic (i.e., highly cooperative) H-bond breaking must wait until  $100^{\circ}\text{C}$  is reached (at 1 atm). Looking at the problem of the existence of liquid water from the vantage point of the ice crystal, we can say that the problem is to explain why hydrogen-bond breaking occurs in two separate cooperative processes.

The helix-coil transition displayed by polypeptides (and polynucleotides) is a cooperative process involving the breakage of hydrogen bonds which is understood. The one-dimensional character of this phenomenon has permitted exact evaluation of the partition function for a realistic model for the possible states of the whole cooperative polymer molecule. Agreement of the various, virtually equivalent, treatments<sup>(2, 3, 4)</sup> of this problem with experimental results has been excellent. It may, therefore, be instructive to take a closer



**Fig. 1.** Schematic diagram of the alpha helix. When, for example, the three hydrogen bonds *d*, *e*, and *f* bridging the residue 7 are broken, rotation is possible around the chemical bonds in this residue, allowing it to assume nonhelical postures.

look at the physical interpretation implicit in the mathematical theory of this transition (although this “transition” is imperfectly sharp) to see if any clue can be obtained concerning our problem of the two-stage breaking of H bonds in the three-dimensional case at hand.

In the case of the polypeptide helix-coil transition, the basis of the cooperativity is easily described.<sup>(2, 3, 4)</sup> Beginning at one end of the  $\alpha$ -helical chain, let us label the sequence of hydrogen bonds, *a*, *b*, *c*, *d* and the sequence of amino acids 1, 2, 3, 4, etc. (Fig. 1). Then, in this  $\alpha$ -helical structure we see that H bond *e* closes a ring involving what would otherwise be rotatable C–C bonds of amino acids, 6, 7, and 8; H bond *f* closes 7, 8, 9, etc. There is, thus, a network of interconnected rings. Focusing attention on amino acid 7, we see that the rotations around its C–C bonds are restricted by its involvement in three rings, those closed by H bonds *d*, *e*, and *f*. All three of the latter must be broken if rotation around the C–C bonds of amino acid 7 are to occur. Terms in the partition function involving, for example, the breakage of *e* alone among the set *d*, *e*, and *f* will tend to carry little weight, for they represent an expenditure of energy (small Boltzmann factor) in return for which no rotational entropy (no degeneracy factor) has been gained. Terms involving the breakage of both *d* and *e*, but only *d* and *e*, among the set *c*, *d*, *e*, and *f* will be even more suppressed in the partition function, for in these cases two H-bond energy units have been paid with no entropic return. Terms involving isolated breakage of an adjacent trio, e.g., breakage of *d*, *e*, and *f* with *c* and *g* intact, will be somewhat less suppressed, in the appropriate temperature range, for one amino acid rotational entropy unit (that of amino acid 7) has been gained for the expenditure of the three units of H-bond energy. Once this has been accomplished, however, a roughly equal amount of extra entropy can be gained by breakage of only one more H bond, either *c* or *g*, for the breakage of four adjacent H bonds releases two amino acids from the ring constraints. Furthermore, the breakage of five adjacent H bonds releases three amino acids from ring restraints, six releases four . . . , and *j* releases *j* – 2. Thus, whereas we have difficult “nucleation” of so-called random-coil regions, we have easy growth of these regions. At temperatures where any H bonds at all are broken, relatively long strings of broken H bonds will tend to be formed; the mag-

nitudes (governed by degeneracies and Boltzmann factors) of the various terms in the partition function reflect this situation.<sup>(2, 3, 4)</sup>

What we can learn from this situation that may be applicable in our three-dimensional problem is clearly that the breakup of orderly interconnected small rings of interaction carries a cooperative entropic component.<sup>5</sup> In the melting of ice we may also expect cooperative entropic effects associated with the breaking of orderly interconnected small rings. It is thus tempting to postulate that the breaking of these may be the principal process involved in melting. This suggestion has the virtue of providing part of an answer to the puzzle alluded to above—the incompleteness of melting as a process of breaking H bonds (i.e., the fact that melting is not sublimation). It portrays melting as a cooperative process of breaking ordered small rings which, though it may go to completion as a proper cooperative process should, does not require the breaking of all the H bonds; highly branched structure (containing ring closures at random<sup>6</sup>) persists and constitutes the liquid phase.<sup>7</sup>

To make the analogy with the helix-coil situation more tractable, we outline here another way of representing it. Although we do not pursue here the quantitative results already obtained by the more complete methods,<sup>(2, 3, 4)</sup> we do demonstrate the existence of the “transition,” this being our current principal concern. Before proceeding with this, however, we note that two questions are posed by the postulate we are now pursuing: (1) Would hydrogen bonds which are not parts of small rings indeed persist above a temperature high enough (0°C at 1 atm) to break orderly interconnected small rings? (2) If they do persist at higher temperatures, would their ultimate breakup also be

<sup>5</sup> Consideration of the polynucleotide helix-coil transition yields somewhat similar conclusions. Using the familiar analogy between the DNA double helix and a (twisted) ladder, we see that each pair of adjacent (base pair) “rungs” of the ladder forms, in conjunction with the two included (ribosephosphate) side rails, a small closed ring, when both adjacent potential base pairs are paired through the Watson-Crick H bonds. The breakup of these H bonds on heating involves a cooperativity which is partly entropic in origin. Thus, in addition to an energetic cooperativity associated with the breaking of “stacking” interactions, there is an entropic cooperativity associated with the fact that, as originally pointed out by Stockmayer and Jacobson, [H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.* **18**, 1607 (1950)], the rotational entropy of a ring increases much faster than linearly with the size of the ring. When a base pair originally at the interface of helical and randomly looped regions rotates out of the helical posture, it increases the size of the loop on its “random-loop” side by joining the latter. The larger the latter was originally, the more entropy it gains by the accretion of the new base pair. Thus, we have another cooperative effect associated with the breakup of H bonds in rings.

<sup>6</sup> The random coil “phase” of polypeptides (and polynucleotides) certainly involves configurations possessing ring closures as well as pure chain configurations. It is only the ordered array of small rings characteristic of the  $\alpha$ -helix that is lost on the transition from helix to random coil.

<sup>7</sup> The fact that the liquid state is characterized in any instant by essentially one cluster, or “network,” will be seen below via the gelation analogy to condensation.

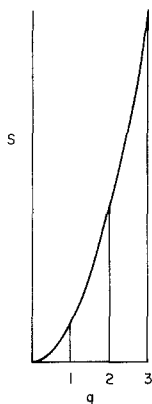


Fig. 2. The entropy  $S$  per site is built up quadratically as the bonds holding that site fixed are broken. In ref. 2, the entropy per site is zero until  $q = 3$  where it takes its maximum value (step function).

cooperative (vaporization)? These questions, taken in the inverse order, are the subjects of the next two sections. The reader whose interest lies primarily in our qualitative considerations may wish to pass directly to them.

The main difference between the formulation of helix "melting" to be presented now and the familiar ones<sup>(2, 3, 4)</sup> outlined above is that, whereas in the previous treatments no entropy is assumed to be gained until all three of the bonds capable of fixing an amino acid (site) are broken, in the treatment considered below the entropy per site is assumed to be built up progressively (quadratically) as these bonds are broken (see Fig. 2). The contribution, to the configurational partition function, of an amino acid for which  $q$  of these bonds ( $0 \leq q \leq 3$ ) are broken is then

$$\exp -\beta u(q) = Z^{q^2} \exp -\beta q \epsilon = \exp -\beta q (\epsilon - \beta^{-1} \ln Z^q) \quad (1)$$

where  $\ln Z^{q^2}$  is the entropy associated with an amino acid when  $q$  of the bonds restricting it are broken,  $\beta^{-1} = kT$ , and  $\epsilon$  is one-third of the energy associated with a broken H bond. The configurational partition function for a helix with  $N$  amino acid sites is now written as

$$Q_N = \sum_{\{n\}} g(\{n\}) \exp \left( -\beta \sum_{q=0}^3 n_q u(q) \right) \quad (2)$$

where  $n_q$  is the number of sites with  $q$  broken bonds and  $g(\{n\})$  is the number of linear arrangements of bonds for a given set  $\{n\}$  with the restriction  $\sum_q n_q = N$ .

In the spirit of Ising-model calculations we assign a number  $\sigma_{\alpha, i}$  to each pair  $i$  of fourth-neighbor amino acids which enclose site  $\alpha$  and specify that  $\sigma_{\alpha, i} = 0$  for an intact H bond and  $\sigma_{\alpha, i} = -1$  for a broken H bond at  $\alpha, i$ . The number of broken H bonds in any configuration is then given by

$$R = -\frac{1}{3} \sum_{\alpha, i} \sigma_{\alpha, i} \quad (3)$$

where the sum over  $i$  goes from 1 to 3, and the sum over  $\alpha$  from 1 to  $N$ . Using Eq. (1) we can write

$$\sum_{q=0}^3 u(q)n_q = \varepsilon \sum_{q=0}^3 qn_q - \beta^{-1} \ln Z \sum_{q=0}^3 q^2 n_q \quad (4)$$

By defining the new variable  $s_{\alpha,i} = 2\sigma_{\alpha,i} + 1$ , so that  $s_{\alpha,i} = 1$  if there is an intact H bond at  $\alpha, i$  and  $s_{\alpha,i} = -1$  if there is not, we find

$$\sum_{q=0}^3 qn_q = - \sum_{\alpha,i} \sigma_{\alpha,i} = \frac{3}{2}N - \frac{1}{2} \sum_{\alpha,i} s_{\alpha,i} \quad (5)$$

and

$$\begin{aligned} \sum_{q=0}^3 q^2 n_q &= - \sum_{\alpha,i} \sigma_{\alpha,i} + 2 \sum_{\alpha,i < j} \sigma_{\alpha,i} \sigma_{\alpha,j} \\ &= 3N - \frac{3}{2} \sum_{\alpha,i} s_{\alpha,i} + \frac{1}{2} \sum_{\alpha,i < j} s_{\alpha,i} s_{\alpha,j} \end{aligned} \quad (6)$$

Equation (6) is obtained by enumeration. Using Eqs. (4-6), we can rewrite the configurational partition function Eq. (2) as

$$Q_N = \exp \left[ -\frac{3}{2} \beta N \varepsilon - 3N \ln Z \right] \sum_{(s)} \exp \left\{ \left( \frac{1}{2} \beta \varepsilon - \frac{3}{2} \ln Z \right) \sum_{\alpha,i} s_{\alpha,i} + \frac{\ln Z}{2} \sum_{\alpha,i < j} s_{\alpha,i} s_{\alpha,j} \right\} \quad (7)$$

Equation (7) has the well-known form of the partition function for the Ising model.<sup>(5)</sup> In the one-dimensional case, the "transition" which it displays is not perfectly sharp (except in the limit  $\ln Z \rightarrow \infty$  and  $\beta \varepsilon \rightarrow \infty$ ).

On generalizing Eq. (7), obtained for the one-dimensional problem (helix-coil "transition"), to the corresponding three-dimensional problem (melting of ice), we would expect a sharp transition temperature, in accordance with familiar experience with this equation in its application to other Ising problems. Such a generalization is not, however, straightforward. The cooperativity that we have suggested above for the ice-melting process is one between hydrogen bonds which when intact are responsible for small ring closures and when broken provide the system with a configurational entropy gain. The form of this proposed cooperativity in the three-dimensional case remains an unresolved question. If we assume, for example, that it is principally the six-membered ring pattern in ice that is destroyed upon melting, then we may assume that the contribution to the partition function due to the entropic cooperativity retains the essential features of the aforementioned one-dimensional problem. We can then assign a contribution to the partition function analogous to Eq. (1) to each molecule for which  $q$  of the six-membered

rings in which it might be restrained are broken. A formulation similar to the one presented above would then lead to a three-dimensional Ising model which would exhibit a transition from a state of many six-membered rings to one containing only very few. It is important to note that in this transition the (fractional) change in the total number of H bonds is actually rather small. The key point is the distinction between the breaking of ring-closing H bonds, with which a large entropy increase is associated, and the breaking of others, with which a smaller entropy increase is associated if the pressure is high enough (see Sec. 4). We identify this ring-breaking transition with melting.<sup>8</sup>

### 3. LIQUID-VAPOR EQUILIBRIUM AND THE ANALOGY OF GELATION

The next question that we are faced with is whether the breakup of a randomly branched structure can also be cooperative. This question is best considered from the viewpoint of its inverse, that of the formation of such structure. Looked at this way, the question immediately elicits an affirmative answer, for it is well known that a branching system can display a discontinuity. Nuclear-fission bombs and explosive gaseous chemical reactions are particularly well-known examples of branching systems which display such discontinuities (in time). In the case of branching processes in space, a particularly good example of a discontinuity is the gel point displayed in the "three-dimensional" polymerization of polyfunctional monomers.

The close analogy between the Flory-Stockmayer theory<sup>(6,7)</sup> of gelation and the Mayer<sup>(8)</sup> cluster theory of vapor-liquid equilibria was pointed out by Stockmayer long ago—and apparently overlooked by all except Scatchard *et al.*<sup>(9)</sup> and Gordon *et al.*<sup>(9)</sup> who discussed (respectively) the vapor pressures of H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O mixtures and the liquid miscibility of H<sub>2</sub>O-benzene mixtures. For an H-bonded condensing system, the analogy to gelation should be particularly close because the discrete character of the propensity of (for example) a water molecule to form H bonds (up to four of them) exactly parallels the integer-value property of the number of chemical bonds emanating from any polyfunctional unit in chemical polymerization.

We show here that the Flory-Stockmayer (FS) statistical theory of gelation can be transcribed into a statistical-mechanical theory of condensation for systems with large directional forces such as H-bonding systems. The independent variable in the FS theory is the extent of reaction  $\alpha$ . In our case the analogous quantity is the fraction of OH groups (or lone pairs of electrons) in the whole system which are participating in H bonds. In the case

<sup>8</sup> It is interesting to note that Perram and Levine [*Mol. Phys.* **21**, 701 (1971)], using a tetrahedral lattice model for water and a cooperativity of bond formation of mathematical form similar to that in Eq. (1) but with no distinction between bonds involved in rings and bonds which are not, obtained a transition from a state of many bonds to one containing very few. They associated their transition with a liquid-vapor transition, but it could equally be associated with a solid-vapor transition.



of reversible condensation, we need in effect to relate this quantity to a pair of thermodynamic variables such as temperature and volume (or pressure).

We consider a system of  $N$  elementary units (e.g., water molecules) which can bond together to form polymeric complexes (including unbonded monomers) and let  $m_n$  be the number of  $n$ -mer complexes ( $1 \leq n \leq N$ ). The  $m_n$  are related to the total number of molecules by

$$N = \sum_n n m_n \quad (8)$$

and to the number of complexes by

$$M = \sum_n m_n \quad (9)$$

The major assumption of the FS theory of gelation is that ring formation can be ignored. We shall see that this is a poor approximation for discussion of properties of the liquid (the gel in FS theory). It does not, however, prevent the theory from displaying the essential features of the sol-gel (vapor-liquid) transition. Since our purpose is to show that the formation (or breakup) of branched structures is cooperative by itself, this approximation serves our needs. If there are no rings, each  $n$ -mer contains  $n-1$  hydrogen bonds, and the potential energy attributable to hydrogen bonds is then

$$V_{\text{HB}}(\{m_n\}) = -\varepsilon \sum_n (n-1)m_n = -\varepsilon(N-M) = -\varepsilon(zN\alpha/2) \quad (10)$$

where  $\varepsilon$  is the binding energy of an H bond and  $z$  is the "functionality" of the monomer units (4 for water).

For a given value of  $N$ , the number of ways that  $m_1$  monomers,  $m_2$  dimers, . . . , and  $m_n$   $n$ -mers can be formed is<sup>(7)</sup>

$$\Omega_N(\{m_n\}) = N! \prod_n (w_n/n!)^{m_n} (1/m_n!) \quad (11)$$

where  $w_n$  is the number of ways in which  $n$  units may form an  $n$ -mer without ring formation. The quantity  $w_n$  is given by<sup>(7,9,10)</sup>

$$w_n = z^n (zn - n)! / (zn - 2n + 2)! \quad (12)$$

<sup>9</sup> Strictly speaking, this Stockmayer formula for  $w_n$  requires modification to account for the indistinguishability of the two OH groups and of the two lone pairs of electrons in each of the water molecules which serve as the units in our case. Appropriate numerical modification has been provided by H. Porosoff.<sup>(10)</sup> The modification does not affect the qualitative results of this section.

<sup>10</sup> This Stockmayer formula for  $w_n$  specifies ways of connecting  $n$  monomer units to make an  $n$ -mer. Multiplicity associated with the possibility that each such topologically distinct species may possess a variety of different conformations is not included in  $w_n$ . Since our use below of the DiMarzio-Gibbs<sup>(12)</sup> modification of the Flory-Huggins<sup>(12)</sup> procedure for counting configurations of nonintersecting polymers on a lattice also ignores this possibility, we are assuming here that each topologically distinct  $n$ -mer possesses only one conformation around which it may, however, vibrate internally (see footnote 18). Electrostatic calculations by Porosoff<sup>(10)</sup> and Ben-Naim and Stillinger (see footnote 15) suggest that the potential governing internal rotation around a hydrogen bond possesses one broad minimum at the symmetrical-eclipsed orientation and one broad maximum.

If we were to consider only the hydrogen-bonding contribution to the potential energy, then, using (10), (11), and (12), we would obtain a partition function of the form

$$Q/N! = (v/\lambda^3)^N \sum_{\{m_n\}} (V/v)^M [\Omega_N(\{m_n\})/N!] \exp[-\beta V_{\text{HB}}(\{m_n\})] \quad (13)$$

where  $V$  is the volume of the system and  $\lambda = (\beta h^2/2m\pi)^{1/2}$  is the thermal wavelength of the molecules. (The inclusion of  $\lambda$  assures that the kinetic energy is always  $\frac{3}{2} kT$  per molecule.) The quantity  $v$  is a measure of the volume of the attractive part of the potential energy. Using Eq. (13), we would find, not unsurprisingly, that the system undergoes a collapse. The collapse occurs when the extent of H bonding is precisely the same as the critical extent of reaction which characterizes the gel point of the FS theory. The source of this collapse is easily seen. We have totally neglected the effects of the hard-core repulsion of two molecules which approach one another too closely. It is well known that a similar collapse occurs if the repulsive term in the van der Waals equation is omitted. Indeed the vapor-liquid phase transition (with its accompanying critical point) is properly viewed as a consequence of the interplay of attractive and repulsive forces. Therefore, we must incorporate the effects of repulsions into our analysis.

Lattice models<sup>(11, 12)</sup> have proven to be extremely useful in the treatment of repulsions in condensing systems. In particular, the use of a lattice model allows us to utilize the Flory-Huggins procedure<sup>(12)</sup> in calculating the number of ways of placing polymers on a lattice without allowing them to intersect. For each distribution of Eq. (11), the number of ways of placing that distribution on the lattice is<sup>(12)</sup>

$$P(N_0, \{m_n\}) = [N_0! / N_0^N (N_0 - N)!] \{ [N_0 z(z-1)]^M / z^{m_1} (z-1)^{m_1+m_2} \} \\ = [1/(1 - N/N_0)^{N_0-N}] \prod_n [A_n N_0 z(z-1) e^{-n}]^{m_n} \quad (14)$$

<sup>11</sup> Perhaps the best way of introducing lattice models of fluids is through the cell-hole theory (CHT) [see T. Hill, *Statistical Mechanics* (McGraw-Hill Book Co., Inc., New York, 1956) Chaps. 7 and 8]. In CHT the partition function has the form

$$Q/N! = (1/\lambda^{3N}) \sum_{\text{config.}} e^{-\beta N_{AA} u(a)} \prod_{i=1}^N v_i$$

where  $N_{AA}$  is the number of nearest-neighbor pairs and the sum is over all possible configurations of  $N$  molecules on a lattice of  $N_0$  sites with multiple occupation excluded. The term  $u(a)$  is the value of the intermolecular potential evaluated at the nearest-neighbor distance, and  $v_i$  is the "free volume" of particle  $i$  in the configuration.

In the usual treatment of CHT a combinatorial factor  $\Gamma(N_0, \{n_j\})$  is introduced, and the sum is taken over all possible distributions of molecules  $\{n_j\}$  with  $j$  nearest-neighbor vacant cells. In terms of our polymer variables, with neglect of rings and with identification of  $N_{AA}$  as the number of hydrogen-bonded neighbors, we write  $N_{AA} = N - M$  and  $u(a) = -\epsilon$ . Thus, setting  $v_i = v_c$  (the volume of the unit cell) we can write  $Q$  as

$$Q/N! = (v_c/\lambda^3)^N \sum'_{\{m_n\}} \Gamma(N_0, \{m_n\}) \prod_n [\exp \beta \epsilon (n-1)]^{m_n}$$

where the primed sum is taken over all sets of  $m_n$  which satisfy equation (8). We then obtain equation (15) by setting  $\Gamma = \Omega P/N!$

where the second line is obtained with Stirling's approximation and with  $A_1 = [z(z - 1)]^{-1}$ ,  $A_2 = (z - 1)^{-1}$ , and  $A_i = 1$  for  $i \geq 3$ .

We can thus write the partition function, including effects of repulsions, as

$$Q/N! = (v_c/\lambda^3)^N (1 - N/N_0)^{N-N_0} \sum_{\{m_n\}} \prod_n (1/m_n!) [1/n!] \times A_n N_0 z(z - 1) w_n e^{-n+\beta\epsilon(n-1)} m_n \tag{15}$$

where  $v_c$  is the volume of the unit cell. The sum in Eq. (15) may be approximated by its maximum term, for which  $m_n$  is given by

$$\bar{m}_n = N_0 [A_n z(z - 1) w_n / n!] e^{-\gamma n + \beta\epsilon(n-1)} \tag{16}$$

where  $\gamma$  is a Lagrange multiplier determined by the restriction that Eq. (8) be satisfied.

Stockmayer was able to evaluate sums of the general form of  $\sum_n \bar{m}_n$  and  $\sum_n n \bar{m}_n$  in terms of the variable  $\alpha$ . In our case  $\gamma$  can be expressed in terms of  $\alpha$ , and then the second sum essentially gives the density ( $\rho = N/N_0$ ) as a function of  $\alpha$  and  $T$ .<sup>12</sup> This equation can be inverted to give  $\alpha$  (and hence  $\gamma$ ) as a function of  $\rho$  and  $T$ . We obtain an equation of state by differentiating the free energy  $A$  [i.e.,  $-kT \ln(Q/N!)$ ] with respect to the volume. This straightforward but tedious calculation gives

$$\beta P v_c = -\ln(1 - \rho) - \rho + \rho_M \tag{17}$$

where  $\rho_M = (1/N_0) \sum_n \bar{m}_n$  is given by a complicated function of  $\rho$  and  $T$ .

Equation (17) can also be obtained from a grand canonical ensemble via the method of steepest descent.

Equation (17) possesses a coexistence (i.e., phase transition) curve and a critical point; the coexisting phases are a high-density phase (liquid) and a low-density phase (vapor) which correspond, respectively, to high (gel) and low (sol) number of hydrogen-bonded pairs. This is the major result of this section.

Several further comments are in order. Equation (17) cannot be very accurate. It does not yield the correct behavior either at moderately low densities or in the weak coupling (small  $\beta\epsilon$ ) limit. This defect can be remedied by replacing<sup>13</sup>  $e^{\beta\epsilon}$  by  $e^{\beta\epsilon} - 1$ . A more serious defect is that, as a result of the total neglect of rings, the equation of state (17) cannot represent the high-density (i.e., liquid) region.

<sup>12</sup> We have used  $A_n = 1$  for all  $n$  in our calculations. The correct values of  $A_1$  and  $A_2$  should contribute importantly only at densities much smaller than the critical density.

<sup>13</sup> Recently, we have found that this replacement arises naturally out of careful consideration of the role of kinetic (as well as potential) energy in the definition of a cluster bond.

These considerations have nevertheless served our purpose of demonstrating that the breakup of a branched structure is both cooperative and qualitatively consistent with the properties of the liquid-vapor transition. It should be particularly noted that, according to this analysis of condensation via gelation theory, the liquid, at any instant, is indeed essentially one branched structure.

#### 4. FURTHER COMMENTS ON THE PHASE TRANSITIONS

The analogies noted to polymer phenomena suggest that our gel picture for liquid water is capable of accounting for the existence of the two phase transitions (melting and boiling). The arguments presented in Secs. 2 and 3 suggest that the essence of melting lies in the disruption of small, orderly interconnected rings of hydrogen bonds and that the essence of boiling lies in the breakup of an extensively branched random network. It has been shown that each of these processes, taken by itself, is cooperative. It remains to be argued that these processes do indeed occur separately under appropriate conditions.

Now it is only when the total volume into which partially depolymerized fragments can escape is large (low-pressure conditions) that the breakup of random branching yields as much entropy as does the opening of small rings, for it is only in this case (sublimation) that the increase in translational entropy associated with the breakage of non-ring-closing bonds is comparable to or greater than the increase in internal rotational (and librational) entropy associated with the openings of rings. Under higher pressures the first cooperative process encountered on heating ice (identified with melting) will not include the breaking of bonds which are not parts of rings since the translational entropy which might be gained on breaking such bonds would be less than that gained on ring opening (whereas the energy changes associated with these two types of breakage should be nearly the same). The triple point occurs at an intermediate pressure at which the entropy gained on opening small rings is comparable to that gained on breaking non-ring-closing bonds.

The principal process which occurs as the liquid is heated or cooled between 0 and 100°C (at 1 atm) must be the alteration of the number and nature of closed rings. Looking at the liquid from either the vantage point of fusion or that of condensation leads to this conclusion.

From the viewpoint of condensation we can see that, even if we can ignore ring formation in the interpretation of the essence of the vapor-liquid transition, we cannot avoid it in the interpretation of what occurs on further cooling in the pure-liquid range, for not many more interconnections (H bonds) are possible in the gel (liquid) without ring closure. Therefore, unless we insist on completing our model of the liquid in a fashion which will yield a heat capacity for the liquid that is much too small, we see that we cannot ignore ring closure. If, on the other hand, we do not insist on ignoring ring closure during condensation, we come to the same conclusion, for it is still

true that all the sol (vapor) will not have been converted to gel (liquid) until the capacity to form H bonds which do not close rings has been saturated. When all the vapor has been condensed, the only types of potential H bonds which remain to be formed on further cooling in the pure liquid are ring-closing ones, the formation of which must therefore be primarily responsible for the large heat capacity of the liquid.

From the viewpoint of fusion, a similar conclusion can be reached. Even if we suppose that fusion involves essentially no net breakage of non-ring-closing bonds (as suggested by our discussion of fusion above and demanded by our liquid-gel analogy drawn from consideration of condensation), we are faced with the conclusion that, unless the liquid at the melting point contains ring closures, the maximum average H-bonded coordination number cannot exceed 2,<sup>14</sup> so that at least half of the H bonds would have to have been broken on melting. The supposition that such a large fraction of the H bonds of ice are broken on melting yields a heat of fusion significantly larger than that observed, unless the H-bond energy is chosen as unreasonably less than the "spectroscopic value" of about 2.6 kcal-mole<sup>-1</sup>. Allowance for loops in the randomly branched network removes this difficulty and should certainly permit good fits to the known heats of fusion and vaporization with a reasonable choice for the hydrogen-bond energy.

## 5. PROPERTIES OF LIQUID WATER IN VIEW OF PROPOSED MODEL

### 5.1. Radial Distribution Function

The radial distribution function indicates that an average oxygen atom in liquid water has between four and five nearest-neighbor oxygen atoms between 2.8 and 2.9 Å away, next-nearest neighbors predominantly between 4.3 and 5.2 Å away, and some small excess density of neighbors between 6.2 and 7.5 Å away. Now, an infinitely long linear chain structure composed of water molecules H-bonded together with H-bond lengths of 2.85 Å and angles between adjacent H bonds of  $\cos^{-1}(-\frac{1}{3})$ , i.e., the tetrahedral angle, provides each water molecule with two nearest neighbors 2.85 Å away and two next-nearest neighbors 4.7 Å away. If, as calculations of the electrostatic interaction between H-bonded water molecules suggest,<sup>(10)</sup> the symmetrical eclipsed configuration<sup>15</sup> with respect to rotation around H bonds is significantly

<sup>14</sup> This is true for branched chains lacking ring closures as well as for linear chains.

<sup>15</sup> This configuration is defined as follows. Consider the partial plane which is bounded on one edge by a line drawn through the O-H---O axis of the hydrogen bond in question and within which lies the off-axis OH bond of the water molecule which is the proton donor in this H bond. Consider also the partial plane which is bounded by the same hydrogen-bond axis and within which lies the bisector of the two off-axis OH bonds of the water molecule which is the electron pair donor to the H bond. In the symmetrical-eclipsed configuration the dihedral angle between these two partial planes is 180°. See A. Ben-Naim and F. Stillinger, in *Water and Aqueous Solutions*, R. A. Horne, ed. (Wiley-Interscience, New York, 1972), p. 295.

preferred, there will also be an excess population density centered about 6.8 Å away.

The additional two to three nearest neighbors at distance between 2.8 and 2.9 Å cannot be fully accounted for as H-bonded nearest neighbors even with allowance for a reasonably large number of closed rings to increase the average H-bonded coordination number, for the total number of nearest neighbors in the 2.8–2.9 Å range (*ca.* 4.5) exceeds even that in ice. However, the mean separation of two non-H-bonded near-neighboring oxygen atoms is also expected to fall between 2.8 and 2.9 Å since the van der Waals radius of an oxygen atom is *ca.* 1.4–1.5 Å. (Indeed, in the structure of ice-VIII there are eight nearest neighbors at a distance of 2.86 Å, only four of which are H-bonded to the central molecule.) The fact that this coincidence has been ignored has apparently been responsible for the often-made assumption that virtually all water molecules must be in ice-like environments. The random network or “gel” model to which we have been led in the preceding discussion is consistent with the radial distribution function, and there is no need for further structural assumptions.

## 5.2. Infrared and Raman Spectra

Possibly the most discussed feature in the infrared and Raman spectra of liquid water, studied as a function of temperature, is the appearance of isosbestic points in several groups of absorption bands associated with proton motions.<sup>(13)</sup> We accept the point of view that these points provide strong evidence that the OH groups in liquid water exist in effectively two discrete states in mutual equilibrium and that these states are related to the presence of broken and intact hydrogen bonds.

Several facts have emerged from the spectral investigations of isosbestic points in water:<sup>(13, 14)</sup>

- (a) The fraction of water molecules not involved in hydrogen bonding (i.e., monomeric water) is probably less than 1% and can be ignored.
- (b) The fraction of molecules having no more than one OH group involved in a hydrogen bond increases with increasing temperature.
- (c) At low temperature the spectrum of liquid water bears some resemblance to that of ice.

These facts are not inconsistent with the model proposed here. In consideration of fact (c), one must recognize that infrared and Raman spectra are not particularly sensitive to the finer details of structure. This observation is supported by the very close similarity of the spectra of linear and branched hydrocarbons and those of polyethylenes with varying degrees of crosslinking.

### 5.3. Static Dielectric Constant and Dielectric Relaxation Time

The dielectric constant of water is unusual not only in the largeness of its static value but also in the narrowness of its dispersion, which behaves like that of a single mode of motion. With regard to the former, we limit our remarks here to the qualitative observation that the random gel model provides the local correlations between angular coordinates of molecules which, according to the theory of Kirkwood,<sup>(15)</sup> are requisite to a large dielectric constant. If most of the correlations that are lost on melting are those associated with small rings, the dielectric constant would not be expected to change dramatically on melting, since dipole-moment vectors in rings tend to cancel out.

With Haggis *et al.*<sup>(16)</sup> and in conformity with the accepted mechanism for dielectric relaxation in ice,<sup>(17)</sup> we attribute the single dielectric relaxation time in water to a mode of motion in which doubly hydrogen-bonded molecules (Bjerrum "DL fault" pair in the case of ice) reorient via rotation around one hydrogen bond with requisite breakage of the other. In the gel model the equilibrium population of doubly hydrogen-bonded molecules cannot be negligible. The energy of activation for such a mode of motion should be approximately the energy of one hydrogen bond, i.e., *ca.* 3 kcal-mole<sup>-1</sup>. Curvature in the experimentally observed Arrhenius plot somewhat obscures simple analysis, but the value of 3 kcal-mole<sup>-1</sup> is cited by Haggis *et al.* as yielding rough correspondence with the relaxation time and its temperature dependence.

We must now ask why molecules which are singly, triply, or quadruply hydrogen-bonded to the rest of the gel network do not give rise to observed relaxations. The spinning, around its single H bond, of a singly H-bonded molecule should be associated with infrared frequencies. Indeed, the value of the dielectric constant (*ca.* 5) on the high-frequency side of the relaxation at 10<sup>-11</sup> sec (which we have attributed to doubly H-bonded molecules) is still significantly larger than the square of the refractive index measured at optical frequencies, indicating the presence of another dispersion somewhere in the infrared region.

The triply and quadruply H-bonded molecules fail to yield observable dispersions for another reason. In these cases the frequencies of relaxation would certainly fall in the range of dielectric measurements, but the intensities associated with these relaxations would be small. In the case of a triply bonded molecule, relaxation by rotation around one H bond requires the breakage of the other two and a consequent activation energy of at least 6 kcal-mole<sup>-1</sup>, which yields a relaxation time about 100 times larger than that required for the relaxation of a doubly bonded molecule. Long before an appreciable fraction of this longer time has expired, the three branches defining a particular molecule as triply H-bonded will have been snipped away by the relaxation of doubly H-bonded molecules: A triply H-bonded unit does not remain triply

bonded long enough to relax as a triply bonded unit. The same argument applies *a fortiori* to the relaxation of quadruply H-bonded molecules, which would be slower than that of doubly H-bonded molecules by a factor at least  $10^4$ .<sup>16</sup>

#### 5.4. The Density Maximum at 4°C

The conventional interpretation of the shrinkage of molar volume between 0° and 4°C at 1 atm attributes this to a decrease in the number of tetrahedrally coordinated water molecules, to each of which an abnormally large molecular volume is attributed. The interpretation of this abnormally large molecular volume of 4-coordinated units need not be sought in the peculiarities of any particular tetrahedral lattice as a whole; it can be expressed in the idea that, if four molecules are located in four very special positions around a central one it may be difficult for as many others (not H-bonded to the central one) to get as close to the central one as they could if all were free to accommodate themselves to the best geometry for a coordination number higher than 4. Thus it would seem to make little difference for the interpretation of the volume-temperature behavior whether these tetrahedrally H-bonded water molecules are presumed to exist together in ice-like structures or presumed to occur at random in a gel-like structure of the type we are proposing here.

One should note that the process which gives rise to this contractile component on heating is not restricted to a narrow range of temperatures (such as 0–4°C) but rather exists over a wide range extending from low temperatures in the supercooled liquid to *ca.* 30°C. That this is true can be seen by subtracting from the total curve of volume vs temperature the monotonically increasing curve which one may expect to arise from increasing amplitudes of vibration of molecules in any fixed configuration, i.e., the thermal expansion one sees in a glassy or crystalline state. When the latter is subtracted, the remainder of the  $V$ - $T$  behavior, attributable to configurational changes in the liquid, exhibits a (broad) minimum not at 4°C but rather at about 30°C.

#### 5.5. The Supercooled Region and the Glassy State

The speed of the relaxation mechanism in liquid water, discussed above, facilitates nucleation of ice crystals and, in practice, prevents extensive supercooling. Nevertheless the properties of the metastable supercooled

<sup>16</sup> It might be thought that this argument leads to the conclusion that the dielectric relaxation time in ice ought to be only  $10^4$  times longer than that in water, as compared with the factor  $10^6$  actually observed. However, the effect of the rotation in ice is to convert a molecule which originally participated in four H bonds into one which participates in two H bonds and two high-energy faults (Bjerrum D and L faults), which may then be expected to travel apart via rotation of the molecules forming the other halves of the faults. This situation has been discussed by others [N. Bjerrum<sup>(17)</sup> and L. Onsager and M. Dupuis, *Electrolytes*, B. Pesce, ed. (Pergamon Press, London, 1952)] and need not be pursued further here.



liquid, even in the range where they are not directly observable in practice, need to be confronted by any theory.

In the cases of liquids which can be extensively supercooled, a transformation to a glassy phase is normally observed. If extensive supercooling could be achieved in the case of liquid water, a transition to glassy water would presumably be observed. Support for this point of view is provided by the successful production of amorphous water by a vapor-deposition technique.<sup>(18)</sup>

In and below the temperature region of the glass transition, not even internal metastable equilibrium can be attained in a liquid in reasonable times. Nevertheless, even the hypothetical thermodynamic properties, estimable by extrapolation below the glass transition of equilibrium data obtained above it, are of first importance.

Such extrapolations<sup>(19)</sup> show clearly that the ultimate fate of the metastable equilibrium liquid on extensive cooling is *not* continuous conversion to the crystal. They show that the liquid, sufficiently supercooled, will have lost all its excess (as compared to the crystal) entropy at a temperature (well above absolute zero) where its energy is still much larger than that of the crystal. That this temperature represents some sort of ground state (which may be highly degenerate *per mole* and still yield a negligible entropy) for the amorphous phase was recognized by Gibbs,<sup>(20)</sup> who used this recognition as the basis of a theory for equilibrium properties of polymers. His postulate of an empirical correlation between this reference temperature, where the configurational entropy is essentially zero, and the glass temperature, where the relaxation time becomes longer than the duration of an experiment (a reasonably well-defined temperature in spite of variations in the durations of experiments because the relaxation time is a rapidly varying function of temperature in this range), was developed by Gibbs and DiMarzio.<sup>(20)</sup> This latter correlation was provided with an interpretation by Adam and Gibbs<sup>(21)</sup> who succeeded in showing a way in which configurational entropy, in a temperature region in which it is in short supply, can be the predominant factor in the determination of relaxation times.

The success of this body of theory in accounting for the influence of molecular weight, composition (in the case of copolymers), concentration (in the case of "plasticized" polymers), crosslinking, etc., on the glass transition and, indeed, in accounting for the fact that the glass transition (a kinetic property) always falls below the melting point (a thermodynamic property), as well as in accounting for the quantitative nature of the variation in relaxation time on the approach to the glass transition (the so-called WLF equation), indicates that its implications concerning the nature of glass-forming liquids other than polymers should also not be ignored. The theory ascribes the dearth of configurational entropy and consequent glassification to the absence of spherical molecular symmetry in glass-forming liquids. In cases where this asymmetry is particularly marked, as in linear or branched polymers, the glass-transition temperature is found, both theoretically and experimentally,

to be high (*ca.*  $300 \pm 100^\circ\text{K}$  for many noncrosslinked polymers).<sup>17</sup> In the case of a liquid composed of small molecules with a propensity to form a hydrogen-bonded network, it should be moderately high, as is the case for glycerol and (putatively) water.

## 6. SUMMARY AND CONCLUSIONS

The considerations of Secs. 2–4 have provided an interpretation of the phase transitions which distinguish liquid water from ice and water vapor and have thereby provided the essence of a physical model for liquid water. The possibility that the model thus obtained can account for the “peculiar” properties of water within the liquid range has been discussed briefly in Sec. 5, where it is seen that, if difficulties are eventually to emerge, they are not so obvious as to be recognizable at this time.

In this article the problems posed by the two phase transitions have been neither formulated in totally satisfactory ways nor analyzed completely. The effects of intracluster vibrations, for example, are yet to be considered.<sup>18</sup> It would be most surprising, however, if the two-transition feature were to be lost upon more careful treatment of the basic concepts introduced here. Inasmuch as the problem of accounting for two transitions (let alone one!) is of long standing, these concepts merit further examination, both with regard to the phase transitions and with regard to the nature and properties of liquid water.

The model for the liquid which our considerations of the phase transitions strongly suggest is that of a random (constantly rearranging) gel. The term “gel” is intended to convey the concept that, at any instant (time interval  $<10^{-11}$  sec for water), the liquid consists essentially of a cluster (hydrogen-bonded in this case) of macroscopic size, in analogy to this use of the term in polymer physical chemistry (where the bonds are chemical and more persistent).

This model is consistent with that indicated by the computer-simulated molecular dynamics effected by Rahman and Stillinger.<sup>(22)</sup> On inspecting pictorial representations of their results, one is unable to identify an appreciable number of small ring closures unless one adopts absurdly liberal definitions of “hydrogen bond” and “ring.” This conforms with the proposition posed here to the effect that it is primarily the ordered small rings of the

<sup>17</sup> If the polymer chains are stiff, in an appropriately defined sense,<sup>(20)</sup> or if they are cross-linked, the configurational entropy is especially small and the glass temperature especially high.

<sup>18</sup> An approach to this, somewhat analogous to that of G. Némethy and H. Scheraga [*J. Chem. Phys.* **36**, 3382 (1962); **41**, 680 (1964)], has been given by H. Porosoff.<sup>(19)</sup> He found that the thermodynamic properties in the liquid phase are particularly sensitive to the intramolecular vibrations. For the purposes of this paper, one should view the parameter  $\epsilon$  introduced in Sec. 3 as a *free* energy associated with a hydrogen bond.

crystal that are lost on fusion. Both the Rahman–Stillinger computations and our considerations of concepts which will account for two phase transitions thus indicate that clusters<sup>19</sup> in the liquid are more disordered than has sometimes been supposed. They both also suggest, on the other hand, that these clusters are far larger<sup>20</sup> than has often been supposed.

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<sup>19</sup> In this paper we have ignored the component of energetic cooperativity arising from the putative nonpairwise additivity of hydrogen-bond formation [H. S. Frank and W.-Y. Wen, *Dis. Faraday Soc.* **24**, 133 (1957)]. Such an effect should operate in the direction of sharpening the profiles of the two phase transitions, the existence of which as true transitions (discontinuities) we have been at pains to interpret here. Furthermore, in principle, at least, such an effect can be incorporated into the gelation analysis.

<sup>20</sup> This feature is an implicit assumption of the model of J. A. Pople [*Proc. Roy. Soc.* **A205**, 163 (1951)]. It can also be obtained from lattice-gas (Ising) models for the condensation of simpler liquids<sup>(5,11)</sup> and of water (P. D. Fleming and J. H. Gibbs, to be published).

## DISCUSSION

**Professor G. S. Kell** (*National Research Council, Ottawa*). Perhaps you could clarify a point for me. There are four bond directions at each vertex, giving six pairs of bonds, and in hexagonal ice this means that 12 six-member rings pass through the vertex. When the broken rings are counted, it is found that breaking a single bond breaks many rings—in this example one broken bond breaks 6 six-member rings. Rather than talk about rings, it is going to be simpler and more economical to talk about broken bonds as people have all along. Yet, Pauling showed 30 years ago that only one quarter of the bonds disappear from ice on melting. Perhaps at the end of your paper you backed down a little from the extreme position taken at the starting point. Still it appears that at high temperatures, at least, your liquid must show essentially 2-coordination. Are you not, by such emphasis on topological considerations, in danger of getting in the position where it is said that liquid water is essentially the same thing as solid alcohol, which contains linear, hydrogen-bonded chains?

**Professor Gibbs** (*Brown University, Providence, Rhode Island*). I need to make several points clearer to answer this many-faceted question:

Firstly, the value 2 for the average H-bonded coordination number is correct, even at high temperatures, only in the absence of ring closures. With allowances for ring closures it is found to be larger.

Secondly, even an average coordination number as small as 2 doesn't imply purely linear chains. They may be highly branched, as only ring closures can increase it to values above 2.

Thirdly, I discussed the hypothetical case of condensation without ring closures simply to show that the essence of this transition is not dependent on ring closing. In this way, I could demonstrate simply how it happens that, under appropriate conditions, we observe two disparate phase transitions—one (condensation) associated *essentially* with the formation of a randomly branched network or "gel" and the other (freezing) associated *essentially* with the formation of an ordered array of small rings.

Now, my fourth observation is that we know we shouldn't carry this viewpoint to the extreme of failing to recognize that ring closures at random must accompany the infinite branching process which nonetheless appears to be the essence of the discontinuous, or phase transition, character of condensation. On purely intuitive grounds, one expects a highly branched structure to display numerous "accidental" ring closures. It would have to pay a heavy entropy price to avoid many of them and simply cannot avoid them all. Indeed, a pure Cayley tree (no ring-closing bonds) cannot be contained in space. Recent developments in the treatment of gelation address these difficulties with techniques of "percolation" theory. Although these go beyond our immediate purposes here, we still should note that they are related to the difficulties that we have found in our approach to condensation via simple gelation theory. Mathematically, these difficulties are manifestations of problems associated

with an assumed analytic continuation of the sums of infinite series beyond their circle of convergence (that is, beyond the zero-density gel point). Physically, these difficulties are almost certainly attributable to our neglect of ring closures.

My fifth point is a reminder that, even if ring closures could be totally ignored in an approximate discussion of condensation, they could not be ignored in even a qualitative discussion of what ensues on further cooling, for, once gelation (condensation) has occurred, all water molecules are (at any instant) part of the same cluster (the “gel”), and only *intragel* H bonds remain to be formed. Cooling in the liquid range will introduce many ring closures and markedly increase the average H-bonded coordination number, although, for the reason I have given in discussing the radial distribution function, there is no apparent need to assume that it becomes as large as 4.

For my sixth and last point, I want to confront the part of Kell’s question which dealt with melting and note that his formulation of this part of the question contains the key to the answer. The very fact that breaking one hydrogen bond in the ice structure destroys many six-membered rings ensures that only rather few hydrogen bonds need to be broken in order to destroy all the hexagonal rings. If this were not true, we would indeed be stuck (in our theoretical concepts) with an average H-bonded coordination number for the liquid which would be too small to be consistent with Pauling’s interpretation of the observed heat of fusion.

**Professor G. Némethy** (*Université de Paris-Sud*). It seems to me that by neglecting all interactions between nonbonded molecules, you are throwing out completely any analogy with liquid argon.

**Professor Gibbs**. We do not totally ignore them. I did not talk about this in order to keep the presentation simple. When a Flory–Huggins lattice is used, not only can the repulsions be accounted for, but, in a very rough way, a nondirectional kind of attraction can also be taken into account. Simply, every time a lattice site is left empty, it costs a certain amount of “hole” energy. This is a very crude way of introducing another interaction in addition to the hydrogen bonds.

**Professor Némethy**. Still, if you do not account for directional interaction between the molecules, you will not get actual condensation, either in the case of argon or of water, especially of the non-hydrogen-bonded molecules.

**Professor Gibbs**. You can if you want to. To pursue this kind of treatment in cases where hydrogen bonding does not exist, you obviously cannot neglect the weaker interactions because you have to have something to serve as the basis for “gelation” (or condensation), but you do not have to assume that these interactions are directional.

We obtained condensation just from reversible gelation theory, which *per se* doesn’t require directional bonding.

What gelation theory does require (in addition to saturability of bonding) is the approximation contained in the two-state concept for a “bond,” i.e.,

an intact state and a broken state as opposed to a continuous potential. It is in this sense (and in the neglect of rings) that it differs from its otherwise close cousin, the Mayer cluster integral expansion, and represents a *quantitatively* less reasonable way of describing argon condensation. It is also in this sense that it bears a resemblance to an Ising model (of which the lattice gas is one version) and appears much more tractable than Mayer cluster theory for a case like water.

Now, in our treatment the specification that H bonding is directional actually enters only when the lattice is introduced. Without the lattice we have no repulsions in the theory, but we get condensation. In fact, we get too much condensation in this case! Without the lattice repulsions the liquid-vapor equilibrium curve never terminates at a critical point.

It is interesting to note that the lattice device is often used not only just to account for repulsions (and directionality of bonding), as here, but also (in place of cluster or gelation theory) as the means of enumerating attractive interactions (by assigning them to nearest-neighboring site occupiers). When this is done, one has the so-called "lattice-gas" version of the Ising model, which, in spite of its directional character, has most often been applied to argon!

**Professor Némethy.** You said that the liquid-vapor equilibrium corresponds to the condition that the average functionality is 2, leading to gelation. Is this a sufficient condition?

**Professor Gibbs.** Only if you make Stockmayer's assumption that, as the clusters are growing in the gas phase, ring closures can be ignored. This corresponds, in the Mayer cluster theory, to ignoring all irreducible cluster integrals  $\beta$  except  $\beta_1$ . This is an enormous simplification, but it still has the transition in it.

**Professor Némethy.** If you allow for the absence of ring closures by introducing only  $\beta_1$ , don't you need a critical concentration?

**Professor Gibbs.** There is a particular vapor density associated with each temperature on the liquid-vapor equilibrium curve and a "critical" one at the critical point, just as with the experimentally observed phenomena.

**Professor H. S. Frank** (*University of Pittsburgh*). If you are giving a new proposal for water structure, you should not get away without saying how the maximum of density is accounted for, and I am going to do just that for you. I am going to propose something that I got some years ago from Morrison up at Ottawa, who said that he had been toying with the idea that the shrinkage on warming of water is analogous to the shrinkage on warming of rubber. The analogy seems sound statistically, and the only thing that kept him from believing it was the fact that the hydrogen bond in water breaks too often, and this, as a matter of fact, is one of your difficulties. You have been giving comparisons with polymers in which there are honest bonds that live a long time compared to the lifetime for reorientation of the water molecule, which Professor Hertz has been telling us is  $10^{-11}$  sec. We cannot use this analogy,

therefore, unless we can count on a water molecule turning around and coming back to the same place. If this can be achieved, then you can have your rubber stretching.

**Professor Gibbs.** This raises a point I should clarify. As long as a bond persists for enough vibrations, then, as far as the thermodynamics are concerned, you can treat the system in the way I have described. What we do is say that we have all different kinds of clusters, all different kinds of topologies and shapes, etc., that we put on the lattice. Now, as the system flows in time it makes no difference for the thermodynamics whether a cluster of shape *A* originally in one location and a cluster of shape *B* originally in another location interchange places by diffusion or whether *A* and *B* simply change into *B* and *A*, respectively, by breaking bonds and forming new connections. In the theory for equilibrium properties, all that matters is that I sum over all possible states, that is, all kinds of shapes in all kinds of locations. But you are right in your observation that it is necessary for the validity of such a model that bonds persist for a time long compared to the periods of important intracuster vibrations.

One other thing your question brings to mind is that, although we have had in mind an interpretation of the density maximum, this phenomenon is the one thing among all the things we have looked at which has not yet fallen out of our model in a rather natural way. I should not be surprised if we should come to like your suggestion on this point better than the more-or-less conventional one that we have invoked.

**Professor P. A. Giguère** (*Université Laval, Canada*). Let me point out that any explanation for the density maximum of ordinary water at 4°C must also account for the important fact that in heavy water the temperature range of increasing density is nearly double, *viz*, from 3.8 to 11.5°C.

May I also make one last remark regarding hydrogen peroxide. The melting point of that crystal is very close (−0.4°C) to that of ice in spite of a nearly double molecular mass. Now, the packing forces are quite the same in both crystals, namely, four hydrogen bonds per molecule. However, in ice these forces are much better balanced (tetrahedral about each oxygen atom) than in hydrogen peroxide (one unengaged orbital on each oxygen atom). This makes for a less stable structure.