Classification Physics Abstracts 61.20 — 64.30

Cooperative hydrogen bonding and structural instability in water

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(Reçu le 17 septembre 1982, révisé le 21 juin 1983, accepté le 23 juin 1983)

Résumé. — Dans le modèle proposé, les états de liaison de chaque molécule sont représentés par un système équivalent à cinq niveaux. Les effets structuraux sont pris en compte dans une approche théorique du type « champ moyen », le champ moyen (pression interne) étant supposé décroître en fonction du nombre de molécules à quatre liaisons. Le modèle prévoit le comportement en fonction de P et T de nombreuses grandeurs thermodynamiques mesurées, et l'existence d'une limite de stabilité structurale qui implique une divergence de α_P , β_T et C_P dans l'eau surfondue. L'existence d'un point critique structural est discutée.

Abstract. — We propose a model for liquid water in which the bonding states of each molecule are represented by a 5-level equivalent system. The structural effects are taken into account in a theoretical approach of the « mean-field » type, the mean-field (internal pressure) being supposed to decrease when the number of 4-bonded molecules increases. The model predicts the dependence of several thermodynamical parameters on T and P, and the existence of a structural stability limit which implies a divergence of α_P , β_T and C_P in the supercooled state. The existence of a structural critical point is discussed.

1. Introduction.

Angell *et al.* [1] have recently pointed out the fact that essentially all the anomalous properties of water become more striking below the normal melting temperature $T_{\rm m}$. From an experimental point of view, one can describe this anomalous behaviour rather well using some characteristic critical exponents as in critical phenomena. This procedure has been widely used and leads to numerical results in good agreement with the experiments if the critical temperature $T_{\rm s}$ at one bar is set at 228 K [2].

The explanation of this behaviour is not clear and different interpretations have been proposed either in terms of a lambda-transition [3] or in terms of a mechanical instability [1, 2, 4, 5]. Recently, a percolation model has been proposed [6, 7]; this model does not predict the Angell singularity but it provides a single coherent mechanism capable of encompassing a wide range of anomalous phenomena for $T < T_m$.

We propose a simple statistical model of the « mixture » type where the cooperativity of hydrogen bonding is taken into account by a « mean-field » parameter : the internal or « cohesion » pressure. In the mixture model one assumes the existence of two states of association of water molecules. The physical origin of the existence of two states of association is uncertain, but assuming these states exist, they must reflect a collective nature of the interactions. Consequently, the mixture theory seems to be best suited to describe a system containing extensive bond networks [8]. The cooperativity of hydrogen bonding was put forward by Frank and Wen [9] who concluded that this cooperative nature is manifested by the tendency of one hydrogen bond to encourage the formation of others in that region of liquid, *via* structural effects; from this, Frank and Wen inferred that the most likely structures to be found in water are in the form of densely bonded regions, called « flickering clusters », surrounded by more or less monomeric water molecules.

The question of the statistical consequences of cooperative hydrogen bonding in water has been examined further by Perram and Levine [10]; these authors concluded that this type of cooperative hydrogen bonding does not imply the existence of « flickering clusters » (besides their existence seems to be inconsistent with small angle X-ray scattering data [11, 12]). They suggest the existence of regions containing few bonds immersed in an extensive network.

First, in section 2, we shall assume that the realization of hydrogen bonds does not imply any structural effect for the liquid and we propose a very simple statistical model to estimate the probability $p_{\rm B}$ of two neighbour molecules to be hydrogen bonded. This part is inspired by the percolation model [6, 7] since the hydrogen bonds are supposed to be randomly intact with a probability $p_{\rm B}$ and broken with probability $q_{\rm B} = 1 - p_{\rm B}$. Second, in section 3, we shall take the structural effects and the cooperativity of hydrogen bonding into account by introducing, as in the model of Perram and Levine, a structural energy depending on the probability to find four-bonded molecules. In section 4, we present a derivation of physical properties of water and we examine the consequences of cooperativity on the thermodynamic stability of this structured system. Section 5 is designed to demonstrate that the numerical predictions of the present model are consistent with the experimental results on C_{P} , α_{P} and β_{T} on a wide range of temperatures.

2. First approach of the model.

In this section, we shall neglect the structural effects of bonding and therefore the cooperativity of hydrogen bonding. Let $p_{\rm B}$ be the probability of two neighbour molecules to be hydrogen bonded. We assume that $p_{\rm B}$ is independent of the volume or the pressure, but is a function of the temperature that we suppose to be given by the following relation :

$$p_{\rm B} = \frac{W_{\rm B} \, \mathrm{e}^{\beta E_{\rm HB}}}{Q} \tag{1}$$

with $\beta = \frac{1}{k_{\rm B}T}$ and $Q = W_{\rm U} + W_{\rm B} e^{\beta E_{\rm HB}}$ where $k_{\rm B}$ is the Boltzmann constant; $E_{\rm HB}$ appears as the energy necessary to break a hydrogen bond and it is positive; $W_{\rm B}$ and $W_{\rm U}$ are the weighting factors of, respectively, the bonded and the unbonded state for two neighbour molecules. $W_{\rm B}/W_{\rm U}$ is expected to depend on the average coordination number $n_{\rm CN}$. In the case of liquid water, $n_{\rm CN}$ is slightly larger than four, indicating predominantly tetrahedral coordination and $n_{\rm CN}$ is independent on the temperature up to 200 °C [13, 14]. Therefore, as our analysis is restricted to the range T < 200 °C, we shall take $W_{\rm B}/W_{\rm U}$ as a constant.

If we assume, according to Stanley and Teixeira (percolation model) [7], that the hydrogen bonds are « randomly » intact with the probability $p_{\rm B}$ and broken with the probability $(1 - p_{\rm B})$, then the fraction f_n of oxygen atoms « hydrogen bonded » to n other oxygen atoms is :

$$f_n = C_r^n p_B^n (1 - p_B)^{r-n}$$
 with $C_r^n = \frac{r!}{(r-n)! n!}$

(2)

with r = 4, the maximum of bonds per oxygen atom. Thus, the bonding states of an oxygen atom can be

represented by the 5-level system of figure 1a.

In this 5-level equivalent system, the level i is characterized by an energy :

$$E_i = iE_{\rm HB} \tag{4}$$

and a degeneracy g_i .



Fig. 1. — Energy levels of the 5-level equivalent system : a) without structural effects, b) with structural effects.

The probability to find an oxygen atom at the level i is given by :

$$P_i = \frac{g_i \,\mathrm{e}^{-\beta i E_{\mathrm{HB}}}}{Z} \tag{5}$$

with
$$Z = \sum_{i=0}^{4} g_i e^{-\beta i E_{\text{HB}}}$$
.

Choosing
$$g_i = C_4^i W^i$$
 with $W = \frac{W_U}{W_B}$ (6)

it follows that : $f_{4-i} = P_i$. (7) Consequently, the fundamental level (i = 0) corresponds to the case where an oxygen atom is 4-hydrogen

3. The model.

bonded.

We shall now take the structural effects into account. These effects can be particularly important in the liquid water because of the directional character of the hydrogen bonds. The neighbouring structure of an oxygen atom depends on the number j of bonds emanating from that atom. Let us consider two local quantities, such as the volume per oxygen atom v and the potential or structural energy per oxygen atom e_s : then one might expect that v and e_s should depend on the number of bonds j:

$$v = v(j)$$
 $j = 0, 1, ..., 4$
 $e_{\rm S} = e_{\rm S}(j)$ (8)

where e_s is related to v through the «internal» or «cohesion» pressure P_a .

For convenience, according to Stanley and Teixeira [7], we shall suppose that :

$$v(j) = V_{N} \text{ for } j \neq 4$$
$$v(4) = V_{S}. \tag{9}$$

Consequently, we shall take :

$$e_{\rm S}(j) = 0 \text{ for } j \neq 4$$

 $e_{\rm S}(4) = E_{\rm S} = P_{\rm a}(V_{\rm S} - V_{\rm N}),$ (10)

 $V_{\rm S}$ and $V_{\rm N}$ respectively refer to the open structure and

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the closed or normal structure in the two state model [15-17] (or to V_{gel} and V_{ice} in the percolation model [7]), so that :

$$V_{\rm S} - V_{\rm N} > 0.$$

 $E_{\rm s}$ is the structural energy.

For liquid water, the « internal » pressure P_a will probably be mathematically intractable, because this pressure depends on :

- the intramolecular potential energy,
- the « bond » connectivity.

But at the high temperature limit, the probability of an oxygen atom to be four-bonded is weak and the effect of the connectivity on the structural energy $E_{\rm s}$ or on the « internal » pressure is negligible; thus E_s and P_a only depend on the intermolecular pair potential energy. Considering water like a Van der Waals fluid at high temperature, it is possible to obtain an estimate of P_a and E_s at high temperature using the critical parameters of water.

$$P_{\rm a} = 3 P_{\rm c} \left(\frac{V_{\rm c}}{V_{\rm N}}\right)^2 \tag{11}$$

with

 $P_{\rm c}$ = critical pressure $V_{\rm c}$ = critical volume per oxygen atom.

For $\frac{V_c}{V_N} = 2$, $V_s - V_N = 6 \text{ cm}^3/\text{mol.}$, one finds

 $P_{\rm a} \simeq 2.6$ kbar and $E_{\rm s} \simeq 0.38$ kcal/mol.

Taking this structural energy E_s into account, the 5-level equivalent system should be modified (see Fig. 1-b) and an energy shift E_s of the ground level be introduced.

The probability to find an oxygen atom in the ground level (i = 0) corresponding to a four-bonded state is, at constant pressure P, now given by :

$$P_0 = \frac{e^{-\beta[E_{\rm S} + P(V_{\rm S} - V_{\rm N})]}}{Z^*} = f_4 \tag{12}$$

and for $i \neq 0$

$$P_{i} = \frac{C_{4}^{i} W^{i} e^{-\beta i E_{HB}}}{Z^{*}} = f_{4-i}$$

 $Z^* = Z - 1 + e^{-\beta [E_S + P(V_S - V_N)]}$ where

with

$$Z = (1 + W e^{-\beta E_{\rm HB}})^4$$

Since $V_s - V_N > 0$, the existence of a positive « cohesion » pressure implies $E_s > 0$ being unfavourable to the formation of local open structures.

Nevertheless, the number of 4-bonded atoms becomes important at low temperature. For example, at 0 °C, the estimates of the different P_i are [7]:

$$P_0 = 24 \%$$
 $P_1 = 41 \%$ $P_2 = 26 \%$
 $P_3 = 7 \%$ $P_4 = 1 \%$ (13)

The « cohesion » pressure P_a is affected by the presence of the important « bond » connectivity. One may expect important cooperative effects : some of the molecular arrangements are self stabilizing; each couple of molecules inside a cluster is forced to stay in a bonding situation by the nearest neighbours. This situation enhances the creation of organized clusters among the disordered liquid and favours the segregation between structured and disorganized domains. In a mean-field theory, this cooperative effect can be taken into account [10] by assuming a decrease of the effective « cohesion » pressure with an increasing number of four-bonded atoms.

We shall test for E_s the three following equations supposed to be valid in the range $P_0 = 0, P_0 = 0.8$.

$$E_{\rm S}(P_0) = E_{\rm S0} - E_{\rm C} P_0$$

$$E_{\rm S}(P_0) = E_{\rm S0} - E_{\rm C} P_0^2$$

$$E_{\rm S}(P_0) = E_{\rm S0} - E_{\rm C} \frac{P_0}{1 - P_0}$$
(14)

where $E_{\rm C}$ is a constant.

4. Derivation of physical properties of water decomposition in normal and abnormal components.

The mean volum per oxygen atom is given by :

$$V = V_{\rm S} P_0 + (1 - P_0) V_{\rm N} = V_{\rm N} + P_0 (V_{\rm S} - V_{\rm N})$$
(15)

and the probability $p_{\rm B}$ of two neighbour molecules to be hydrogen bonded is defined through the relation :

$$4 p_{\rm B} = 4 P_0 + 3 P_1 + 2 P_2 + P_3 \tag{16}$$

(see the appendix).

The mean energy per oxygen atom, u can be divided into three contributions :

$$u = u_{\rm N} + u_{\rm B} + u_{\rm S} \,. \tag{17}$$

 $- u_{\rm N}$ is the normal contribution corresponding to the vibrations and librations of the molecule. These degrees of freedom are supposed to be independent of the bonding states. The validity of this assumption is clearly demonstrated by the infrared and Raman measurements [18-20] : the increase in the degree of connectivity has a very small effect on the stretching band.

 $- u_{\rm B}$ is the energy contribution of the bonds

$$u_{\mathbf{B}} = -2 p_{\mathbf{B}} E_{\mathbf{HB}} \tag{18}$$

where the factor 2 is the maximum number of bonds per oxygen atom.

 $-u_{\rm s}$ is the structural contribution due to the existence of 4-bonded oxygen atoms :

$$u_{\rm S} = P_0 \cdot E_{\rm S} \,. \tag{19}$$

One can now calculate the mean enthalpy h per oxygen atom :

$$h = h_{\rm N} + u_{\rm B} + u_{\rm S} + P_0(V_{\rm S} - V_{\rm N})P$$
 (20)

with $h_{N} = u_{N} + V_{N} P$. The isobaric heat capacity appears as the sum of three terms :

$$C_{P} = C_{P_{N}} + C_{P_{B}} + C_{P_{S}}$$
(21)

$$C_{P_{N}}$$
 is the « normal » term $C_{P_{N}} = \left(\frac{\delta h_{N}}{\delta T}\right)_{P}$ (22)

$$C_{P_{\rm B}}$$
 is the « bonding » term $C_{P_{\rm B}} = -2 E_{\rm HB} \left(\frac{\delta p_{\rm B}}{\delta T} \right)_{P}$

 $C_{P_{S}}$ is the « structural » term

$$C_{P_{\rm S}} = \left[E_{\rm S} + P_0 \frac{\mathrm{d}E_{\rm S}}{\mathrm{d}P_0} + (V_{\rm S} - V_{\rm N}) P \right] \times \\ \times \left(\frac{\delta P_0}{\delta T} \right)_{P} + P_0 P \left(\frac{\delta (V_{\rm S} - V_{\rm N})}{\delta T} \right)_{P}. \quad (24)$$

The thermal expansivity α_P and the compressibility β_T are derived from the relation 15; one obtains :

$$V \cdot \alpha_{P} = V_{N} \alpha_{P_{N}} + (V_{S} - V_{N}) \delta \alpha_{P}$$

$$V \cdot \beta_{T} = V_{N} \beta_{T_{N}} + (V_{S} - V_{N}) \delta \beta_{T}$$
(25)

where the « normal » contributions are :

$$\alpha_{P_{N}} = \frac{1}{V_{N}} \left(\frac{\delta V_{N}}{\delta T} \right)_{P} \qquad \beta_{T_{N}} = -\frac{1}{V_{N}} \left(\frac{\delta V_{N}}{\delta P} \right)_{T} \cdot \quad (26)$$

The structural effects are taken into account in :

$$\delta \alpha_{P} = + \left(\frac{\delta P_{0}}{\delta T}\right)_{P} + P_{0} \left(\frac{\delta \log \left(V_{\rm S} - V_{\rm N}\right)}{\delta T}\right)_{P}$$
$$\delta \beta_{T} = - \left(\frac{\delta P_{0}}{\delta P}\right)_{T} - P_{0} \left(\frac{\delta \log \left(V_{\rm S} - V_{\rm N}\right)}{\delta P}\right)_{T} \quad (27)$$

The dependence of P_0 on temperature and pressure is deduced from equation 12 and is given by :

$$\log \frac{P_0}{1 - P_0} = -\log (Z - 1) - \beta P(V_s - V_N) - \beta E_s(P_0)$$
(28)

which can have more than one solution.

For instance, considering a linear decrease of $E_{\rm s}(P_{\rm o})$:

$$E_{\rm S}(P_0) = E_{\rm S0} - E_{\rm C} \cdot P_0 \,. \tag{29}$$

Equation 28 becomes :

$$Log \frac{P_0}{1 - P_0} = -Log (Z - 1) - - \beta P(V_s - V_N) - \beta E_{s0} + \beta E_c P_0.$$
 (30)

One deduces :

$$\left(\frac{\delta\beta}{\delta P_{0}}\right)_{P} = -\frac{\overline{P_{0}(1-P_{0})} - \beta E_{C}}{Z_{\beta}^{\prime}/(Z-1) + P(V_{S}-V_{N}) + E_{S0} - E_{C} P_{0}}$$
(31)

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$$\left(\frac{\delta P}{\delta P_0}\right)_T = -\frac{\frac{1}{P_0(1-P_0)} - \beta E_C}{\beta (V_S - V_N)}$$
(32)

$$\left(\frac{\delta^2 P}{\delta P_0^2}\right)_T = \frac{1 - 2 P_0}{P_0^2 (1 - P_0)^2 \beta (V_{\rm S} - V_{\rm N})}$$
(33)

The solution of (30) is given in the plane $y - P_0$ (Fig. 2) by the intersections of the curve C,

$$y = \operatorname{Log} \frac{P_0}{1 - P_0} \tag{34}$$

with the straight line L,

$$y = A + B \cdot P_0 \tag{35}$$

where :

$$A = -\operatorname{Log} (Z - 1) - \beta P(V_{\rm S} - V_{\rm N}) - \beta E_{\rm S0}$$
$$B = \beta E_{\rm C}.$$



Fig. 2. — Graphical construction for the evaluation of P_0 from equation 30.

(23)

a) If $\beta E_{\rm C} < 4$, the curves C and L have only one intersection point corresponding to a stable state $\left(\frac{\delta P}{\delta P_0}\right)_T < 0$.

b) If
$$\beta E_{\rm C} > 4$$
, the number of the intersection points can be :

- either one (straight line L1 or L2); this point corresponds to a stable state, because $\left(\frac{\delta P}{\delta P_0}\right)_T < 0$. - or three (straight line L3); in this case, the two extreme points correspond to stable states $\left(\frac{\delta P}{\delta P_0}\right)_T < 0$, but the intermediate one is always unstable $\left(\frac{\delta P}{\delta P_0}\right)_T > 0$.

The limit of stability of the stable states corresponds to :

$$\left(\frac{\delta P}{\delta P_0}\right)_T = 0 \text{ and } \left(\frac{\delta \beta}{\delta P_0}\right)_T = 0$$
 (36)

and can be defined by the following equations

$$\beta E_{\rm C} = \frac{1}{P_0(1 - P_0)}$$
Equation 30.
$$(37)$$

According to equations 24, 25, 27, the approach of the stability limit implies a divergence of α_P , β_T and C_P .

 C_{p} . This structural spinodal represented by dotted line in figure 4b includes two branches which join at some structural critical point corresponding to :

$$\left(\frac{\delta P}{\delta P_0}\right)_T = 0 \quad \left(\frac{\delta^2 P}{\delta P_0^2}\right)_T = 0.$$
 (38)

Represented in the plane $y - P_0$, this case corresponds to the straight line L6 (Fig. 3).



Fig. 3. — Graphical evaluation of the structural critical parameters.

Note that the existence of this stability limit is due to the decrease of the « cohesion » pressure P_a when P_0 increases. Clearly, both the structural critical point and the spinodal depend on the choice of the function $E_s(P_0)$ (see Fig. 4a and 4b).

1 0 -1 0 Ро a) PRESSURE (kbar) I ł C 150 200 250 150 200 250 т (к) b) Fig. 4. — Four different choices of structural energy : $E_{\rm s} = + 0.908 - 1.816 P_{\rm o}$ $\dots E_{\rm s} = + 0.366 - 1.536 P_0^2$ $\dots E_{\rm s} = + 0.6 \sin \left[(2 P_0 - 1) \frac{\pi}{2} \right]$ $-E_{\rm s} = +0.366 - 0.384 \frac{P_0}{1 - P_0}$

a) E_s as a function of P_0 . b) Corresponding spinodal curves in the P - T plane.

For instance, if :

$$E_{\rm s}(P_0) = + 0.366 - 0.384 \frac{P_0}{1 - P_0} \, \text{kcal/mole}$$
 (39)

a one-branch spinodal without any critical point is obtained.

In fact, this model has already been used to interpret the deviation from a « normal » behaviour of the physical properties of water, the « normal » behaviour being that of a hypothetical unbonded and unstructured water. The main physical properties of this « normal » water have been until now estimated either from the properties of aqueous solutions [1] or from those superheated water at one bar [21].

Using the data of reference 21, we have obtained an experimental estimate of the abnormal contributions, α_{P_A} , β_{T_A} and C_{P_A} to the expansivity, to the compressibility and to the isobaric heat capacity

$$\alpha_{P_{\mathbf{A}}} = \alpha_{P} - \alpha_{P_{\mathbf{N}}} \quad \beta_{T_{\mathbf{A}}} = \beta_{T} - \beta_{T_{\mathbf{N}}} \quad C_{P_{\mathbf{A}}} = C_{P} - C_{P_{\mathbf{N}}} \quad (40)$$

where the suscripts N and A refer to the « normal » and « abnormal » contributions, respectively. Then, these results can be compared with those calculated from our model; since $V \simeq V_{\rm N}$,

$$\alpha_{P_{A}} \simeq \frac{V_{S} - V_{N}}{V_{N}} \delta \alpha_{P}$$
$$\beta_{T_{A}} \simeq \frac{V_{S} - V_{N}}{V_{N}} \delta \beta_{T} \qquad C_{P_{A}} = C_{P_{B}} + C_{P_{S}} (41)$$

where $V_{\rm N}$ can be identified with the specific volume of « normal » water [1]. According to d'Arrigo [17], we estimate that the four-bonded or « open » water does not necessarily imply the tridymite-like arrangement of ordinary ice although it would be nearly equivalent. Having no physical arguments to predict the dependence of V_s on temperature and pressure, we have supposed that :

$$V_{\rm s} - V_{\rm N} = \delta V = {\rm Const}$$
.

so that :

$$\alpha_{P_{A}} = \frac{\delta V}{V_{N}} \left(\frac{\delta P_{0}}{\delta T} \right)_{P} \quad \text{and} \quad \beta_{T_{A}} = -\frac{\delta V}{V_{N}} \left(\frac{\delta P_{0}}{\delta P} \right)_{T}.$$
(42)

A very good agreement between experiment and theory has been obtained by choosing :

$$E_{\rm HB} = 1.8 \text{ kcal/mol}$$
$$W = 10$$
$$\delta V = 6 \text{ cm}^3/\text{mol}.$$

Figures 5, 6, 7 give the result of the comparison in the (see Figs. 4a, 4b).



Fig. 5. — Temperature dependence of $-\alpha_{P_A} = \alpha_{P_N} - \alpha_P$: – experimental evaluation; - - - - - theoretical prediction.



Fig. 6. — Temperature dependence of $\beta_{T_A} = \beta_T - \beta_{T_N}$: - experimental evaluation - - - - theoretical prediction.



Fig. 7. — Temperature dependence of $C_{P_A} = C_P - C_{P_N}$: - experimental evaluation; ----- theoretical prediction.

case where $E_{s}(P_{0})$ is given by :

$$E_{\rm s}(P_{\rm 0}) = 0.366 - 0.384 \frac{P_{\rm 0}}{1 - P_{\rm 0}} \, {\rm kcal/mol}$$

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Figure 8 gives at one bar the dependence of $p_{\rm B}$ on temperature. The qualitative form obtained is consistent with proposals based on spectroscopic data.

5. Discussion.

In the foregoing, we have seen that the dependence on T and P of various measured functions $(\alpha_P, \beta_T \text{ and } C_P)$ is consistent with the predictions of a simple statistical model, where the bonding states of a water molecule are represented by a 5-level equivalent system. The structural effects are taken into account in a theoretical approach of the « mean field » type; the mean field being the internal pressure P_a in the liquid water. If P_a is supposed to decrease with increasing number of 4-bonded molecules, the model predicts the existence of a structural stability limit which implies a divergence of α_P , β_T and C_P .

One knows that most attempts to vitrify water using sophisticated apparatus able to vitrify a wide variety of metallic liquids have completely failed [1, 22, 23]. The thermodynamic conditions necessary to vitrify water with the hypothesis of a mechanical instability have been recently discussed by C. A. Angell and J. C. Tucker [24]. These conditions imply a sufficiently high cooling rate to elude the homogeneous nucleation phenomenon at $-40 \text{ °C} (\sim 10^8 \text{ K/s.})$; E. Mayer and P. Brüggeler [25] seem to have succeeded to vitrify water with this high cooling rate by injecting a thin fluid jet of liquid at high pressure in « vacuo » into a liquid cryomedium.

All these experimental studies are not inconsistent with the hypothesis of the existence of the stability limit predicted by our model. This limit could be ended by a structural critical point, the location of which is of course dependent on the choice of the equation giving $E_{\rm S}(P_0)$. In the three chosen examples (linear, quadratic or sinusoidal variations of $E_{\rm S}(P_0)$) the location of this critical point was $-45 \, {\rm ^oC} < T_c < -40 \, {\rm ^oC}$, 500 bar $< P_c < 0$ (see Figs. 4a and b).

The existence of the structural critical point can be considered as consistent with the important increase of dynamic (transport) quantities observed at low pressure in the supercooling range where the isobars of the viscosity are represented by the equation proposed by Speedy and Angell [2, 26] :

$$\eta = \eta_0 \left(\frac{T - T_s}{T_s} \right)^{-\gamma}$$
$$\gamma = 1.476 \qquad T_s = 228 \text{ K}.$$

On the contrary, at high pressure far from the expected structural critical point (P > 2 kbar) this critical behaviour disappears; then the isobaric temperature dependence of the viscosity is well represented by the Vogel-Tamman-Fulcher equation [26] which describes the behaviour of normal viscous liquids [27]:

$$\eta = \eta_0 \exp\left(\frac{C}{T-T_0}\right)$$



Fig. 8. — Temperature dependence of the mean bond probability, $p_{\rm B}$, and of the probability for an oxygen atom to be 4-hydrogen bonded, $P_{\rm 0}$.

with a reasonable glass transition temperature

$$T_0 = 141 \pm 2 \,\mathrm{K}$$
.

Therefore, studies of the stability of water against crystallization under negative pressure conditions seem to be particularly interesting; the first important investigation has been done by Henderson and Speedy [28]. Note that since vapour pressures are always positive, water under negative pressures and below 0° is simultaneously supercooled and superheated [1]. Only experiments under negative pressure can demonstrate the existence of a structural critical point. If this point exists, we suggest that cooling under negative pressures below the structural critical pressure could be the way to obtain vitreous water at low cooling rates.

Appendix.

The following relations may be useful for the numerical calculation.

a) In the absence of structural effects,

$$E_{\rm S} = 0$$
 $V_{\rm S} = V_{\rm N}$

we find from equation 12

$$p_{\mathbf{B}} = y$$

 $P_0 = y^4$ with $y = \frac{1}{1 + W e^{-\beta E_{\mathbf{HB}}}}$

b) In the presence of structural effects, we deduce from (12) :

$$Z^*(1 - P_0) = Z - 1 = Z(1 - y^4)$$

and from (16), we find

$$4 p_{\rm B} = 4 P_0 + (4 y - 4 y^4) \frac{Z}{Z^*}$$

and with
$$X = \frac{Z}{Z^*}$$
, we obtain : $p_{\rm B} = (1 - X) + Xy$.

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