

## A SYNERGETIC REPRESENTATION FOR THE DOUBLE-STRUCTURE MODEL OF LIQUID WATER

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The process of self-organization for the double-structure model is introduced and calculated ab initio, in the random-phase approach. Comparison with experiments on heat capacity and other water properties shows a satisfactory correspondence, better than for the previous calculations.

### Introduction

Contrary to its rather simple chemical composition, liquid water has a complicated peculiar structure, which is the topic of several serious investigations [1 — 2]. Despite the simplicity of water, it has unusual properties: abnormal thermodynamic parameters (melting point, boiling point, heat of vaporization, heat of fusion, etc., and all are higher than it would be expected of liquids composed of hydrogen and oxygen), structural properties (maximum density at 4 °C, decrease in viscosity with pressure up to ~ 1000 atm). All these physical abnormalities make water exceptional. These peculiarities determine a lot of unique properties especially concerning the function of living biological matter [2]. Nowadays, there is an increased interest in the problem of possible water structures: from crystalline ice-like one to liquids with various degrees of structural ordering [3 — 7]. The structure of agglomerations of water molecules (in a liquid or solid state) is definitely complicated and exhibits many unusual properties:

- Hydrogen atoms, bonded to one oxygen, can jump over to another oxygen in another water molecule. Thus, a proton makes connection through a lone-pair, bridging oxygen atoms and creating a so-called hydrogen-bridge (which has a much weaker bond strength than normal hydrogen-oxygen bonds).
- Intermolecular dipole interactions and arrangements are not simple due to the above described V-shaped dipole structure.
- Nonregular tetrahedral shape of a water molecule changes the connected hydrogen bridge, so consequently the whole geometric arrangement fluctuates due to fluctuating proton bonds.

- Water-tetrahedra cannot occupy the space as a close packing: voids (holes) between tetrahedra must be present.

Structural division of liquid water into ordered (clustered, type 1) and disordered (type 2) phases is the most widespread model for description. The existence of the clustering of water is revealed by the radial distribution function measured by X-ray diffraction [1]. These measured hydrogen-bridges show that the "ice-structure" does not vanish at once during the melting process. The effect on melting is only that some domains (clusters of water) are disconnected from each other (like islands). With increasing temperature, these domains are gradually broken into the smaller and smaller ones. These domains are not static structures, their size fluctuates but the average is definitely characterizes the actual state. This fact emphasizes the complexity of normal liquid water which mostly can be subscribed to hydrogen-bridges. Numerous models, taking into account these peculiarities, were formulated for liquid-water: the quartz-like structure (based on tetrahedral units) [8], dodecahedral (chlatrate) model (associated with special hydrogen bond rings), bent-hydrogen-bond model (calculates the bent chain of hydrogen bonds) [11] as well as the cluster models: flickering cluster model [12], solid-like model [11], etc. These models reasonably follow the actual systems but fail to yield the density maximum at 4 °C. This means that normal water (obtained by gradual melting from ice) has two structurally different phases: monomer water-molecules and water-clusters (Fig. 1) [12]. Moreover, water clusters in this phase-mixtures can have a large variability depending on their actual structure and phase transitions.

A simple approach assumes the presence of ice-like structures: from simple elements of the structural network to quasi-crystalline ones [3]. The quasi-crystalline structure is formed from the ice-like clustering in consequence of the structure destruction by heating or other disturbances (introduction of admixtures, ultrasound influence, etc.) and is accompanied by an increase in density, change in chemical activity, optical and other properties [4 — 6, 12].

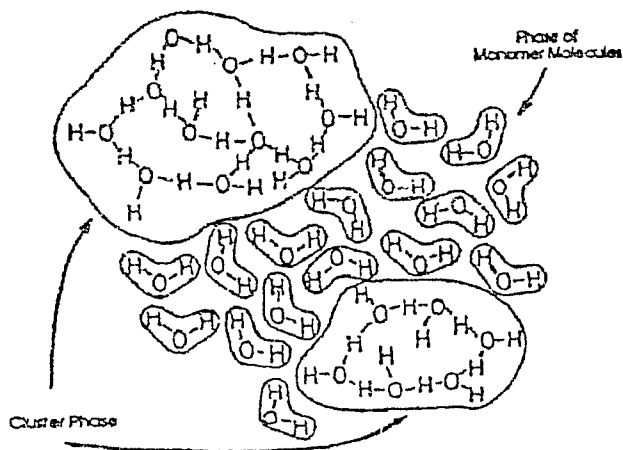


Fig. 1. Two phases of the normal water: monomer molecules and the phase created by clusters

Ordering of water structure has been analyzed. In other models, clusters are tetramers or hexamers [4] with 3 — 4 nm dimensions [3, 5]. The thermodynamic approach to the analysis of such systems needs some restrictions [3, 4] in the case of one- or two-dimensional structures (few layers of H<sub>2</sub>O molecules) as is relevant in biological objects [13].

However, the living system is not an ordered solid. In the biomatter, it is not so trivial to introduce the collective states (contrary to crystals [14]): it is an aqueous solution.

However, water is mostly well ordered in the living state and is nearly crystalline (semi-crystalline [15]). A polarized multilayer of water was described, which can be considered in a quasi-crystalline state, [16].

A great attention has been devoted to the problem of ordered water, enclosing hydrophobic regions and creating inert, osmotically inactive zones [17]. Numerous works point out the importance of ordered water (melted ice) in living objects [18, 19], but a suitable model for these effects does not exist at the time.

In general, the problem to develop an adequate model for water is related to its structure. In our present paper, we describe a model and the process of self-organization in disordered materials. We take into account a number of known facts [3] and our investigations on glassy structures and properties [20] combined with different water-types. The cluster approach to the two-structure model of liquid water using the ideas of synergetics [21, 22] is employed to model the structures and explain the ordering properties of water.

### Model of System

Fluctuations of the order parameter are uniform in homogeneous matter. Under the presence of different

heterophases, various symmetry properties have another physical nature: they determine non-homogeneous fluctuations in macroscopic regions inside the system. All the available sites of the system are occupied by clusters with a probability which defines the actual phase state. The degree of structural disorder is characterized by the actual arrangements, interatomic distances, and space fluctuations in short-range order and by bond angles. We consider the system containing  $N$  atoms which have two states: — disordered states, characterized by significant values of statistical displacement and, as a consequence, anharmonicity of atomic vibrations, shear nonstability, and the possibility of regrouping; — ordered states.

The concentration and stability of disordered states depend on the preparation conditions and initial conditions. Let us suppose that the distribution of atomic positions has the Gaussian form:

$$P(\delta_i) = (2\delta_i Q_i)^{-1/2} \exp(-\delta_i^2/2Q_i).$$

Let us define the average over the random field:

$$\langle \dots \rangle_c = \prod_i \int \dots P(\delta_i) a \delta_i.$$

The average distance  $\langle r_l \rangle_c$  is determined as follows:

$$r_l = \langle r_l \rangle_c + u_l + e_l, \tag{1}$$

where  $u_l$  and  $e_l$  are dynamic and statistical displacements of quasi-equilibrium sites,  $Q_i$  is the distribution parameter which characterizes the disorder in the system,  $\delta_i$  is the longitudinal ( $i = 1$ ) and transverse ( $i = 2$ ) mean-square  $e_l$  deviations, with conditions

$$\langle e_l \rangle_c = 0 \quad \text{and} \quad \langle (e_l)^2 \rangle_c = \sum_i Q_i.$$

The Hamiltonian of the system is

$$H(\{X\}) = \sum_f \sum_l \left( \frac{(P_l^f)^2}{2m} + U_f(r_l) - \mu \right) + \frac{1}{2} \sum_{f,f'} \sum_{l \neq l'} \Phi_{ff'}(r_l - r_{l'}) X_l^f X_{l'}^{f'}. \tag{2}$$

Here,  $X_l^f$  is the local characteristic function, which is determined as

$$X_l^f = \begin{cases} 1 & \text{if the atom } l \text{ is in state } f \\ 0 & \text{if the atom } l \text{ is not in state } f \end{cases}$$

( $f = 1$  corresponds to an ordered state,  $f = 2$  corresponds to a disordered state).

$P_f^i$  is the operator of momentum,  $m$  is the particle mass,  $\mu$  is the chemical potential, and  $U_f = \sum_{f,l'} \Phi_{ff'}(r_l - r_{l'})$  is the one-particle potential, where  $\Phi_{ff'}(r_l - r_{l'})$  is the potential energy of the interaction.

The effective Hamiltonian of the system is

$$\tilde{H} = \int H(\{X\}) d\{X\} = \sum_f H_f,$$

$$H_f = \omega_f \sum_l \left( \frac{(P_l^f)^2}{2m} + U_f - \mu \right) + \frac{\omega_f^2}{2} \sum_{l \neq l'} \tilde{\Phi}_f(r_l - r_{l'}), \quad (3)$$

where  $\omega_f = N_f/N$  is the share of atoms in the  $f$  state;  $N = N_1 + N_2$  and  $\omega_1 = 1 - \omega_2$ . Solving the variational problem in the linear approximation of non-equilibrium thermodynamics gives

$$\delta F / \delta \omega_2 = -a(\omega_2 - \omega_2^c), \quad (4)$$

where the free energy functional

$$F = \sum_f F_{0f} - TS,$$

$$F_{0f} = -\theta \ln \left[ \text{Sp} \left( \exp \left( -\frac{H_f}{\theta} \right) \right) \right], \quad (5)$$

$\theta = kT$ ,  $k$  is the Boltzmann constant,

$S = -k \ln \left[ \prod_f \frac{g_f!}{N_f! (g_f - N_f)!} \right]$  is the entropy,  $g_f$  is the statistic weight of the  $f$  state, and the equilibrium share of disordered states is  $a = (\partial^2 F / \partial \omega_2) \omega_2^c$ .

So we have the functional equation for  $\omega_2$ :

$$\tilde{\Lambda}_2 - \tilde{\Lambda}_1 - 2\tilde{\Phi}_1 + 2\omega_2(\tilde{\Phi}_2 - \tilde{\Phi}_1) -$$

$$-\theta N \left( \ln \left( \frac{g_2}{\omega_2} - 1 \right) - \ln \left( \frac{g_1}{\omega_1} - 1 \right) \right) = a(\omega_2 - \omega_2^c). \quad (6)$$

Let us denote

$$\tilde{\Lambda}_f = \sum_l \left\langle \left\langle \frac{(P_l^f)^2}{2m} \right\rangle \right\rangle, \quad \tilde{\Phi}_f = \left\langle \frac{1}{2} \sum_{l \neq l'} \langle \langle \Phi_{ff'}(r_l - r_{l'}) \rangle \rangle_c \right\rangle, \quad (7)$$

which are the kinetic and potential energies of the corresponding phase states and are averaged over the random field and heterophase fluctuations.

Statistical micro-displacements of liquid particles have to be calculate. To describe the thermal behaviour of the system, we take into account strong anharmonic effects as well as structure transformations.

We apply the self-consistent anharmonic approach, which makes it possible to renormalize the force constants and local potentials as a consequence of the anharmonicity of atomic vibrations [23, 24].

Functional equations, analogous to Eq. (6), for the renormalized force constants  $\tilde{\Phi}_{ll'}^{\alpha\beta}$  and mean-square atomic displacements

$$\tilde{D}_{ll'}^{\alpha\beta} = \langle (u_l^\alpha - u_{l'}^\alpha)(u_l^\beta - u_{l'}^\beta) \rangle$$

$$\frac{\delta F}{\delta \tilde{\Phi}_{ll'}^{\alpha\beta}} = 0, \quad \frac{\delta F}{\delta \tilde{D}_{ll'}^{\alpha\beta}} = 0.$$

Whence,  $\tilde{\Lambda}_f, \tilde{\Phi}_f$  from Eq. (7) and  $\tilde{\Phi}_{ll'}^{\alpha\beta}, \tilde{D}_{ll'}^{\alpha\beta}$  are as follows:

$$\tilde{\Lambda}_1 = \sum_k \frac{\tilde{\pi} w(k)}{4} \text{cth} \frac{\tilde{\pi} w(k)}{2\theta},$$

$$\tilde{\Phi}_1 = \sum_{l,l'} \exp \left\{ \frac{1}{2} \sum_{\alpha,\beta} \tilde{D}_{ll'}^{\alpha\beta} \nabla_l^\alpha \nabla_{l'}^\beta \right\} \Phi_1(r_l - r_{l'}),$$

$$\tilde{\Phi}_{ll'}^{\alpha\beta} = \nabla_l^\alpha \nabla_{l'}^\beta \tilde{\Phi}_1(r_l - r_{l'}),$$

$$\tilde{D}_{ll'}^{\alpha\alpha} = \frac{\tilde{\pi}}{mN} \sum_k \frac{2 \sin^2 \left( \frac{k(r_l - r_{l'})}{2} \right)}{w(k)} \text{cth} \frac{\tilde{\pi} w(k)}{2\theta},$$

$$mw^2(k) = \sum_{l,l'} \sum_\alpha \exp(i k(r_l - l_{l'})) \tilde{\Phi}_{ll'}^{\alpha\alpha} \omega_1, \quad (8)$$

where  $k$  is the wave-vector,  $w(k)$  is the vibrational frequency.

The atomic interaction is written as  $\Phi(r) = \Phi_1(r) + \Phi_2(r)$ . Here,  $\Phi_1(r)$  a long-range term (approximated by the Morse-type potential  $\Psi(r) = V_0(\exp(-12(r-a)/r) - 2 \exp(-6(r-a)/r))$ ) and non-central potential  $G(Z) = G_0 \times \exp(-4(Z/a)^2)$ , where  $Z$  is the deviation of an atom from a plane perpendicular to the bond direction,  $G_0$  and  $V_0$  are parameters of the potentials) and  $\Phi_2(r)$  is a short-range term (approximated by a hard sphere-type potential).

In a self-consistent approach, averaging the interaction potentials (8) over the random field, we get

$$\begin{aligned} \bar{\Psi}(r) &= \omega_1^2 V_0 \exp(\bar{Q}_l) \times \\ &\times (e^{-12(r-a)/r} e^{2Y_l} - 2e^{-6(r-a)/r} e^{Y_l/2}), \\ \bar{G}(z) &= -\omega_1^2 V_0 [1 + 2(Y_l + \bar{Q}_l)]^{-1} \times \\ &\times \exp\left(-\frac{4(z/a)^2}{1 + 2(Y_l + \bar{Q}_l)}\right). \end{aligned} \quad (9)$$

Here  $Y_l = 36 \bar{D}_{ll}/a^2$  and  $Y_t = 4 \bar{D}_{tt}/a^2$  are the average square atomic displacements along the bonding and in the transversal directions;  $\bar{Q}_l = 36 \bar{Q}_l^2/a^2$  and  $\bar{Q}_t = 4 \bar{Q}_t^2/a^2$  are fluctuations of the distance and angle between the bonds,  $a = \langle l \rangle_c = a_0 (1 + \bar{Q}_l/4)$  is the average interatomic distance taking account of the statistical spread of equilibrium sites.

According to the local equilibrium principle of the system, we have  $P = -\frac{zN\omega_1^2 l \bar{\Psi}'(l)}{V}$ , and the average distance is

$$l = a \left(1 + \frac{Y_l}{4} - \delta\right), \quad (10)$$

where  $\delta = \frac{\ln[B(Y_l)/2]}{6}$ ,  $P^* = \frac{PV \exp(\bar{Q}_l)}{6zNV_0}$  is the

reduced pressure,  $B(Y_l) = 1 + \left[1 + \frac{P^* r^2 \exp(Y_l)}{6\omega_1^2 a^2}\right]$ ,  $z$  is the number of the nearest neighbours,  $P$  is the pressure, and  $V$  is the volume.

The potential energy and force constants are defined as

$$\begin{aligned} \bar{\Psi}(r) &= -\frac{\omega_1^2 V_0 e^{-Y_l} e^{-Q_l}}{2} \left[ B(Y_l) - \frac{P^*}{12\omega_1^2} \left(\frac{r}{a}\right)^2 e^{Y_l} \right], \\ \bar{G}(0) &= -\frac{G_0 \omega_1^2}{1 + 2(Y_l + \bar{Q}_l)}, \end{aligned} \quad (11)$$

$$\bar{f}(\theta) = \bar{\Psi}'_l(r) = \omega_1^2 f \left[ \frac{P^*}{12\omega_1^2} \left(\frac{r}{a}\right)^2 + \frac{e^{-Y_l}}{2} B(Y_l) \right],$$

$$f = 72V_0 \exp(-\bar{Q}_l)/a^2. \quad (12)$$

From Eq. (7) and Eq. (8), the kinetic and potential energies are calculated as follows:

$$\omega_1^2 \bar{\Phi}_1(r) = zN [\bar{\Psi}(r) + \bar{Q}(0)]/2, \quad \bar{\Phi}_2 = N\varphi/2,$$

$$\Lambda_f = 3N_f\theta/2, \quad \varphi = \int \rho(r) \Phi_2 dr.$$

Hence, the self-consistent system of Eqs. (6) — (8), (11), (12) takes the form

$$\begin{aligned} \frac{2\omega_1 Y_l}{\tau} &= \frac{e^{Y_l} e^{\bar{Q}_l}}{B(Y_l) + \frac{P^*}{6\omega_1^2} (r/a)^2 e^{Y_l}}, \\ \frac{0.27Y_l\omega_1}{\tau} &= \frac{g}{f} \left[ \frac{(1 + 2(Y_l + \bar{Q}_l))}{\left(\frac{P^*}{12\omega_1^2} (r/a)^2 + B(Y_l)/2e^{-Y_l}\right)^{1/2}} \right], \\ \omega_2 \xi + \omega_1 z &\left\{ \frac{e^{-Y_l} e^{\bar{Q}_l}}{2} \left[ B(Y_l) - \frac{P^*}{12\omega_1^2} \left(\frac{r}{a}\right)^2 e^{Y_l} \right] \right\} + \\ &+ \left\{ \frac{0.1}{1 + 2(Y_l + \bar{Q}_l)} \exp\left(-\frac{4(z/a)^2}{1 + 2(Y_l + \bar{Q}_l)}\right) \right\} - \\ &- \tau \ln \left( \frac{(g_2 - \omega_2)\omega_1}{(g_1 - \omega_1)\omega_2} \right) = a(\omega_2 - \omega_2^e). \end{aligned} \quad (13)$$

Here,  $\tau = \theta/V_0$  is the reduced temperature,  $\xi = \varphi/V_0$  and  $G_0/V_0$  are assumed to be 0.1. The solution for  $\omega_2, Y_l, Y_t$  of the self-consistent system of equations (13) in the temperature range  $T < 100^\circ\text{C}$  was found numerically using the iteration procedure.

The internal energy is

$$E = \omega_1 \bar{\Lambda}_1 + \omega_2 \bar{\Lambda}_2 + \omega_1^2 \bar{\Phi}_1^2 + \omega_2^2 \bar{\Phi}_2^2, \quad (14)$$

and the volume

$$V = N(\omega_1 \nu_1 + \omega_2 \nu_2), \quad (15)$$

where  $\nu_f = \nu_{0f} l_f^3$ , and  $\nu_{0f}$  is a geometric-structural factor. Consequently, the heat capacity  $C_p$  and linear expansion coefficient  $\alpha_T$  are

$$C_p = \frac{1}{N} \frac{\partial(E + PV)}{\partial T} \Big|_p =$$

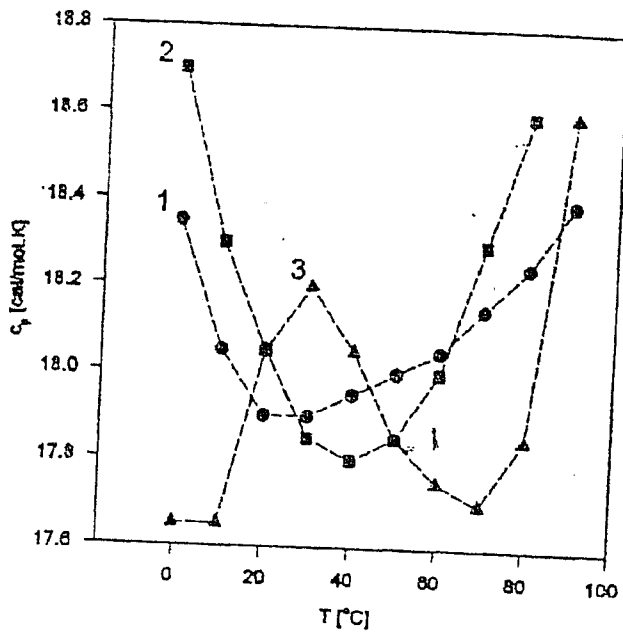


Fig. 2. A comparison of measured and calculated heat capacity of water: (Lines are only the guides for eye.) (1) — experiment, (2) — present calculations, (3) — previous calculations [4]

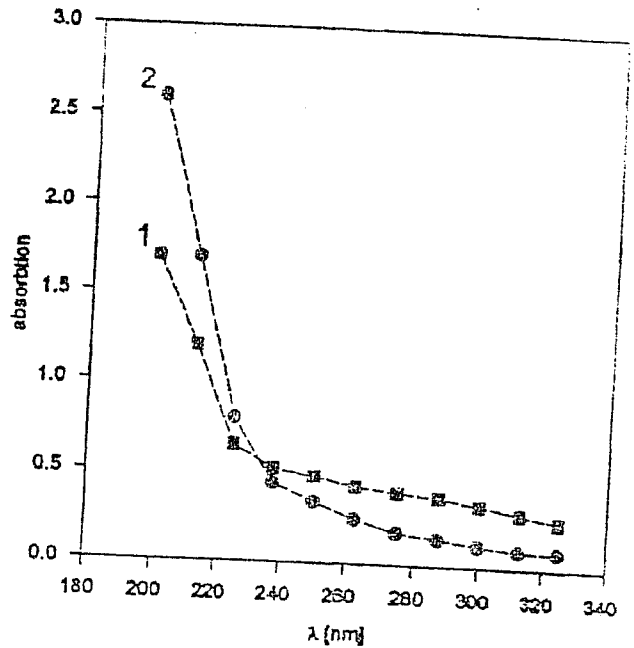


Fig. 3. Optical absorption edge measurements on water (made at room temperature): (Lines are only the guides for eye.) (1) — melted ice → (type 1, water) (2) — boiled at 100 °C and cooled down to room temperature and measured there → (type 2, water)

$$= 3R + \omega_1^2 \frac{\partial(\bar{\Phi}_1/N)}{\partial T} + \omega_2^2 \frac{\partial(\bar{\Phi}_2/N)}{\partial T} + \frac{P}{N} \left( \omega_1 \frac{\partial \nu_1}{\partial T} + \omega_2 \frac{\partial \nu_2}{\partial T} \right) + \frac{1}{N} \{ 2\omega_2 (\bar{\Phi}_1 + \bar{\Phi}_2) - 2\bar{\Phi}_1 + P(\nu_2 - \nu_1) \} \frac{\partial \omega_2}{\partial T}, \quad (16)$$

$$\alpha_T = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_p = \frac{n}{V} (\nu_2 - \nu_1) \frac{\partial \omega_2}{\partial T} + \frac{N}{V} \left\{ \frac{\partial \nu_1}{\partial T} + \omega_2 \left( \frac{\partial \nu_2}{\partial T} - \frac{\partial \nu_1}{\partial T} \right) \right\}. \quad (17)$$

### Results and Discussion

Results of calculations of  $C_p$  according to Eq. (16) are presented in Fig. 2. Parameters  $P^* = 0.1$ ,  $f = 10^5$  erg · cm,  $Q_i = 0.03a$ ;  $a = 2.83$  nm, and  $E = 5$  kcal/mol are taken from [4]. In comparison of experimental and theoretical data including the temperature dependence of  $\alpha_T$  [6], a good agreement is obtained with (17), so the proposed model and approach appear satisfactory.

The nature of the temperature-dependent densification of water may be explained in the frame

of this model: the structural inhomogeneity of liquid in the medium-range order leads to inhomogeneity of phononic subsystems. (Anharmonic atomic vibration is mostly produced by weak bonds.) Vibrational energy (accumulated in clusters) is stored as an elastic deformation energy causing a compression of the system. Anharmonic atomic vibrations for stronger (inter-cluster) bonds become important at higher temperatures, and water expands.

The structural inhomogeneity (degree of order) correlates also with the Urbach tail, namely the slope of the absorption edge decreases with the disorder of the system. Water, as a condensed matter, has electronic excitation at the 7.5 ~ 8.9 eV spectral range ( $x \rightarrow D - B$  transitions [25]). Electron absorption gives the exponential dependence of the extinction coefficient on photon energy and temperature, so the Urbach law is fulfilled [26, 27]. Our measurements were taken on absorption spectra ( $\ln \alpha$  [cm<sup>-1</sup>] dependence on the excitation wavelength  $\lambda$  [nm]) of melted ice and normal water. The sample (water in a special cuvette) was measured using a Hitachi spectrophotometer at room temperature followed by the heating of melted ice up to 100° C and cooling down (Fig. 3). The "normal water" agrees with the actual liquid disorder corresponding to water of type 2. The change of the absorption spectrum shows a more ordered of melted ice (type 1). This was predicted by Eq. (13), which

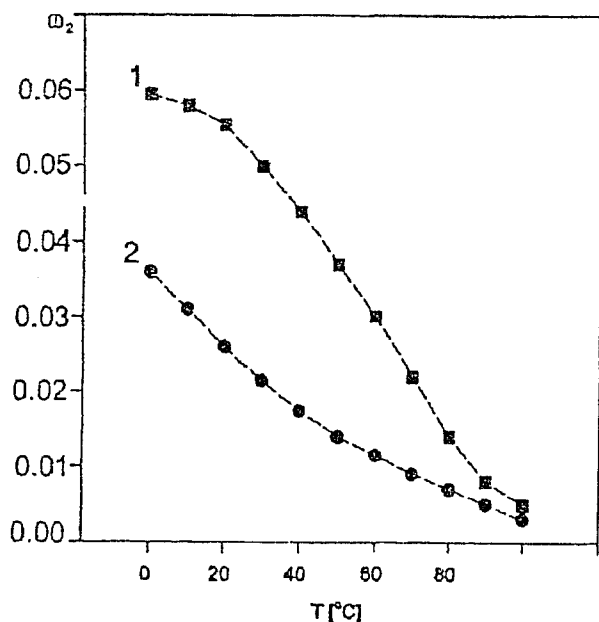


Fig. 4. Temperature dependence of two phases: (Lines are only the guides for eye) (1) — ordered phase, (2) — equilibrium disordered phase

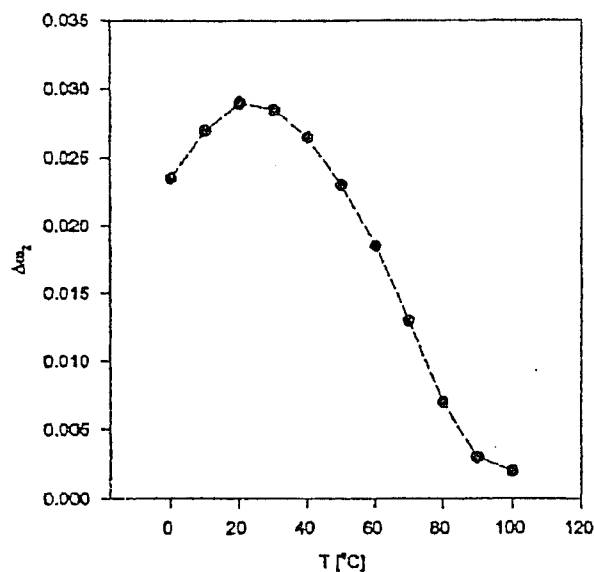


Fig. 5. Destroying the local order by temperature. (Line is only the guide for eye)

gives a decrease in the number of ordered-state clusters when temperature increases.

At a fixed temperature,  $\omega_2 > \omega_2^e$ , where  $\omega_2^e$  characterizes the equilibrium disordered state. The relaxation of the ordered state to the equilibrium one is observed with an increase of the degree of disorder, according

to the results of calculations with Eq. (13) (Fig. 4). This result proves that the ordering effects are those as predicted, and gives the possibility of evaluating the disordering dynamism (Fig. 5) from the difference of two curves (Fig. 4).

Our model is general enough to be extended to the description of a system behaviour in external fields (electromagnetic, ultrasound) that is especially important for investigations of living systems. These studies are in progress.

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