

HIERARCHIC THEORY OF CONDENSED MATTER :

Interrelation between mesoscopic and macroscopic properties

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Materials, presented in this original article are based on:

- [1]. Book by A. Kaivarainen: Hierarchic Concept of Matter and Field. Water, biosystems and elementary particles. New York, 1995 and two of my papers:**
- [2]. New Hierarchic Theory of Matter General for Liquids and Solids: dynamics, thermodynamics and mesoscopic structure of water and ice (see URL: <http://kftt.karelia.ru/~alexk>) and:**
- [3]. Hierarchic Concept of Condensed Matter and its Interaction with Light: New Theories of Light Refraction, Brillouin Scattering and Mössbauer effect (see URL: <http://kftt.karelia.ru/~alexk>).**

Computerized verification of described here new theories are presented on examples of WATER and ICE, using special computer program (copyright, 1997, A. Kaivarainen).

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Summary to Part I of book:
Hierarchic Theory of Matter and Field (by: A. Kaivarainen)

A basically new hierarchic quantitative theory, general for solids and liquids, has been developed.

It is assumed, that anharmonic oscillations of particles in any condensed matter lead to emergence of three-dimensional (3D) superposition of standing de Broglie waves of molecules, electromagnetic and acoustic waves. Consequently, any condensed matter could be considered as a gas of 3D standing waves of corresponding nature. Our approach unifies and develops strongly the Einstein's and Debye's models.

Collective excitations, like 3D standing de Broglie waves of molecules, representing at certain conditions the molecular Bose condensate, were analyzed, as a background of hierarchic model of condensed matter.

The most probable de Broglie wave (wave B) length is determined by the ratio of Plank constant to the most probable impulse of molecules, or by ratio of its most probable phase velocity to frequency. The waves B are related to molecular translations (tr) and librations (lb).

As the quantum dynamics of condensed matter does not follow in general case the classical Maxwell-Boltzmann distribution, the real most probable de Broglie wave length can exceed the classical thermal de Broglie wave length and the distance between centers of molecules many times.

This makes possible the atomic and molecular Bose condensation in solids and liquids at temperatures, below boiling point. It is one of the most important results of new theory, which we have confirmed by computer simulations on examples of water and ice.

Four strongly interrelated new types of quasiparticles (collective excitations) were introduced in our hierarchic model:

1. *Effectons (tr and lb)*, existing in "acoustic" (a) and "optic" (b) states represent the coherent clusters in general case;
2. *Convertons*, corresponding to interconversions between *tr* and *lb* types of the effectons (flickering clusters);
3. *Transitons* are the intermediate $[a \rightleftharpoons b]$ transition states of the *tr* and *lb* effectons;
4. *Deformons* are the 3D superposition of IR electromagnetic or acoustic waves, activated by *transitons* and *convertons*.

Primary effectons (tr and lb) are formed by 3D superposition of the **most probable standing de Broglie waves** of the oscillating ions, atoms or molecules. The volume of effectons (tr and lb) may contain from less than one, to tens and even thousands of molecules. The first condition means validity of **classical** approximation in description of the subsystems of the effectons. The second one points to **quantum properties of coherent clusters due to molecular Bose condensation**.

The liquids are semiclassical systems because their primary (tr) effectons contain less than one molecule and primary (lb) effectons - more than one molecule. *The solids are quantum systems totally because both kind of their primary effectons (tr and lb) are molecular Bose condensates.*
These consequences of our theory are confirmed by computer calculations.

The 1st order [*gas* → *liquid*] transition is accompanied by strong decreasing of rotational (librational) degrees of freedom due to emergence of primary (lb) effectons and [*liquid* → *solid*] transition - by decreasing of translational degrees of freedom due to Bose-condensation of primary (tr) effectons.

In the general case the effecton can be approximated by parallelepiped with edges corresponding to de Broglie waves length in three selected directions (1, 2, 3), related to the symmetry of the molecular dynamics. In the case of isotropic molecular motion the effectons' shape may be approximated by cube.

The edge-length of primary effectons (tr and lb) can be considered as the "parameter of order".

The in-phase oscillations of molecules in the effectons correspond to the effecton's (a) - *acoustic* state and the counterphase oscillations correspond to their (b) - *optic* state. States (a) and (b) of the effectons differ in potential energy only, however, their kinetic energies, impulses and spatial dimensions - are the same. The *b*-state of the effectons has a common feature with **Frölich's polar mode**.

The ($a \rightarrow b$) or ($b \rightarrow a$) transition states of the primary effectons (tr and lb), defined as primary transistons, are accompanied by a change in molecule polarizability and dipole moment without density fluctuations. At this case they lead to absorption or radiation of IR photons, respectively.

Superposition (interception) of three internal standing IR photons of different directions (1,2,3) - forms primary electromagnetic deformons (tr and lb).

On the other hand, the [$lb \rightleftharpoons tr$] *convertions* and *secondary transistons* are accompanied by the density fluctuations, leading to *absorption or radiation of phonons*.

Superposition resulting from interception of standing phonons in three directions (1,2,3), forms **secondary acoustic deformons (tr and lb)**.

Correlated collective excitations of primary and secondary effectons and deformons (tr and lb), localized in the volume of primary *tr* and *lb electromagnetic* deformons, lead to origination of **macroeffectons, macrotransistons and macrodeformons** (tr and lb respectively).

Correlated simultaneous excitations of tr and lb macroeffectons in the volume of superimposed *tr* and *lb electromagnetic* deformons lead to origination of **supereffectons**.

In turn, the coherent excitation of *both: tr and lb macrodeformons and macroconvertions* in the same volume means creation of **superdeformons**. Superdeformons are the biggest (cavitational) fluctuations, leading to microbubbles in liquids and to local defects in solids.

Total number of quasiparticles of condensed matter equal to $4!=24$, reflects all of possible combinations of the four basic ones [1-4], introduced above. This set of collective excitations in the form of "gas" of 3D standing waves of three types: de Broglie, acoustic and electromagnetic - is shown to be able to explain virtually all the properties of all condensed matter.

The important positive feature of our hierarchic model of matter is that it does not need the semi-empiric intermolecular potentials for calculations, which are unavoidable in existing theories of many body systems. The potential energy of intermolecular interaction is involved indirectly in dimensions and stability of quasiparticles, introduced in our model.

The main formulae of theory are the same for liquids and solids and include following experimental parameters, which take into account their different properties:

[1]- **Positions of (tr) and (lb) bands in oscillatory spectra;**

[2]- **Sound velocity;**

[3]- **Density;**

[4]- **Refraction index (extrapolated to the infinitive wave length of photon).**

The knowledge of these four basic parameters at the same temperature and pressure makes it possible using our computer program, to evaluate more than 150 important characteristics of

any condensed matter. Among them are such as: total internal energy, kinetic and potential energies, heat-capacity and thermal conductivity, surface tension, vapor pressure, viscosity, coefficient of self-diffusion, osmotic pressure, solvent activity, etc. Most of calculated parameters are hidden, i.e. inaccessible to direct experimental measurement.

The new interpretation and evaluation of Brillouin light scattering and Mössbauer effect parameters may also be done on the basis of hierarchic theory. Mesoscopic scenarios of turbulence, superconductivity and superfluidity are elaborated.

Some original aspects of water in organization and large-scale dynamics of biosystems - such as proteins, DNA, microtubules, membranes and regulative role of water in cytoplasm, cancer development, quantum neurodynamics, etc. have been analyzed in the framework of Hierarchic theory.

Computerized verification of our Hierarchic concept of matter on examples of water and ice is performed, using special computer program: Comprehensive Analyzer of Matter Properties (CAMP, copyright, 1997, Kaivarainen). The new opto-acoustical device (CAMP), based on this program, with possibilities much wider, than that of IR, Raman and Brillouin spectrometers, has been proposed (see URL: <http://www.karelia.ru/~alexk>).

This is the first theory able to predict all known experimental temperature anomalies for water and ice. The conformity between theory and experiment is very good even without any adjustable parameters.

The hierarchic concept creates a bridge between micro- and macro- phenomena, dynamics and thermodynamics, liquids and solids in terms of quantum physics.

1. The state equation for real gas

The Clapeyrone-Mendeleyev equation sets the relationship between pressure (P), volume (V) and temperature (T) values for the ideal gas containing N_0 molecules (one mole):

$$PV = N_0kT = RT \quad 1$$

In the real gases interactions between the molecules and their sizes should be taken into account. It can be achieved by entering the corresponding amendments into the left part, to the right or to the both parts of eq. (1).

It was Van der Waals who choused the first way more than a hundred years ago and derived the equation:

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad 2$$

where the attraction forces are accounted for by the amending term (a/V^2), while the repulsion forces and the effects of the excluded volume accounted for the term (b).

Equation (2) correctly describes changes in P,V and T related to liquid-gas transitions on the qualitative level. However, the quantitative analysis by means of (2) is approximate and needs the fitting parameters. The parameters (a) and (b) are not constant for the given substance and depend on temperature. Hence, the Van der Waals equation is only some approximation describing the state of a real gas.

We propose a way to modify the right part of eq.(1), substituting it for the part of the kinetic energy (T) of 1 mole of the substance (eq.4.31 in [1, 2]) in real gas phase formed only by secondary effectons and deformons with nonzero impulse, affecting the pressure:

$$PV = \frac{2}{3} \bar{T}_{\text{kin}} = \frac{2}{3} V_0 \frac{1}{Z} \cdot \sum_{tr,lb} \left[\bar{n}_{ef} \frac{\sum_1^3 \left(\bar{v}_{1,2,3}^a \right)^2}{2m(\bar{v}_{ph}^a)^2} (\bar{P}_{ef}^a + \bar{P}_{ef}^b) + \bar{n}_d \frac{\sum_1^3 \left(\bar{v}_d^{1,2,3} \right)^2}{2m(\bar{v}_s)^2} \bar{P}_d \right]_{tr,lb} \quad 3$$

The contribution to pressure caused by primary quasiparticles as Bose-condensate with the zero resulting impulse is equal to zero also.

It is assumed when using such approach that for real gases the model of a system of weakly interacted oscillator pairs is valid. The validity of such an approach for water is confirmed by available experimental data indicating the presence of dimers, trimers and larger H_2O clusters in the water vapor (Eisenberg and Kauzmann, 1975).

Water vapor has an intensive band in oscillatory spectra at $\tilde{\nu} = 200 \text{cm}^{-1}$. Possibly, it is this band that characterizes the frequencies of quantum beats between "acoustic" (a) and "optic" (b) translational oscillations in pairs of molecules and small clusters. The frequencies of librational collective modes in vapor are absent.

The energies of primary gas quasiparticles ($h\nu_a$ and $h\nu_b$) can be calculated on the basis of the formulae used for a liquid (Chapter 4 of [1] or [2]).

However, to calculate the energies of secondary quasiparticles in () and (\bar{b}) states the Bose-Einstein distribution must be used for the case when the temperature is higher than the Bose-condensation temperature ($T > T_0$) and the chemical potential is not equal to zero ($\mu < 0$). According to this distribution:

$$\left\{ \begin{array}{l} a = h\bar{\nu}^a = \frac{h\nu^a}{\exp\left(\frac{h\nu^a - \mu}{kT}\right) - 1} \\ b = h\bar{\nu}^b = \frac{h\nu^b}{\exp\left(\frac{h\nu^b - \mu}{kT}\right) - 1} \end{array} \right\}_{tr,lb} \quad 4$$

The kinetic energies of effectons ()_{tr,lb} and (\bar{b})_{tr,lb} states are equal, only the potential energies differ as in the case of condensed matter.

All other parameters in basic equation (3) can be calculated as previously described [1, 2].

2. New state equation for condensed matter

Using our eq.(4.3 from [1,2]) for the total internal energy of condensed matter (U_{tot}), we can present state equation in a more general form than (3).

For this end we introduce the notions of *internal pressure* (P_{in}), including **all type of interactions** between particles of matter and excluded molar volume (V_{exc}):

$$V_{\text{exc}} = \frac{4}{3} \pi \alpha^* N_0 = V_0 \left(\frac{n^2 - 1}{n^2} \right) \quad 5$$

where α^* is the acting polarizability of molecules in condensed matter (see Part 1 of [3]); N_0 is Avogadro number, and V_0 is molar volume.

The general state equation can be expressed in the following form:

$$P_{\text{tot}} V_{fr} = (P_{\text{ext}} + P_{\text{in}})(V_0 - V_{\text{exc}}) = U_{ef} \quad 6$$

where: $U_{ef} = U_{\text{tot}}(1 + V/T_{\text{kin}}^t) = U_{\text{tot}}^2/T_{\text{kin}}$ is the effective internal energy and:

$$(1 + V/T_{\text{kin}}) = U_{\text{tot}}/T_{\text{kin}} = S^{-1}$$

is the reciprocal value of the total structural factor (eq.2.46a of [1]); $P_{\text{tot}} = P_{\text{ext}} + P_{\text{in}}$ is total

pressure, P_{ext} and P_{in} are external and internal pressures; $V_{\text{fr}} = V_0 - V_{\text{exc}} = V_0/n^2$ (see eq.5) is a free molar volume; $U_{\text{tot}} = V + T_{\text{kin}}$ is the total internal energy, V and T_{kin} are total potential and kinetic energies of one mole of matter.

For the limit case of ideal gas, when $P_{\text{in}} = 0$; $V_{\text{exc}} = 0$; and the potential energy $V = 0$, we get from (6) the Clapeyrone - Mendeleyev equation (see 1):

$$P_{\text{ext}} V_0 = T_{\text{kin}} = RT$$

One can use equation of state (6) for estimation of sum of *all types of internal matter interactions*, which determines the internal pressure P_{in} :

$$P_{\text{in}} = \frac{U_{\text{ef}}}{V_{\text{fr}}} - P_{\text{ext}} = \frac{n^2 U_{\text{tot}}^2}{V_0 T_{\text{kin}}} - P_{\text{ext}} \quad 7$$

where: the molar free volume: $V_{\text{fr}} = V_0 - V_{\text{exc}} = V_0/n^2$;

and the effective total energy: $U_{\text{ef}} = U_{\text{tot}}^2/T_{\text{kin}} = U_{\text{tot}}/S$.

For solids and most of liquids with a good approximation: $P_{\text{in}} \gg [P_{\text{ext}} \sim 1 \text{ atm.} = 10^5 \text{ Pa}]$.

Then from (7) we have:

$$P_{\text{in}} \cong \frac{n^2 U_{\text{tot}}}{V_0 S} = \frac{n^2}{V_0} \cdot U_{\text{tot}} \left(1 + \frac{V}{T_{\text{kin}}} \right) \quad 8$$

where $S = T_{\text{kin}}/U_{\text{tot}}$ is a total structural factor; T_{kin} and V are total kinetic and potential energies, respectively.

For example for 1 mole of water under standard conditions we obtain:

$$V_{\text{exc}} = 8.4 \text{ cm}^3; V_{\text{fr}} = 9.6 \text{ cm}^3; V_0 = V_{\text{exc}} + V_{\text{fr}} = 18 \text{ cm}^3;$$

$$P_{\text{in}} \cong 380000 \text{ atm} = 3.8 \cdot 10^{10} \text{ Pa} \quad (1 \text{ atm} = 10^5 \text{ Pa}).$$

The parameters such as sound velocity, molar volume, and the positions of translational and librational bands in oscillatory spectra that determine U_{ef} (4.3) depend on external pressure and temperature.

The results of computer calculations of P_{in} (eq.7) for ice and water are presented on Fig. 1 a,b.

Polarizability and, consequently, free volume (V_{fr}) and P_{in} in (6) depend on energy of external electromagnetic fields (see Part 1 of [3]).

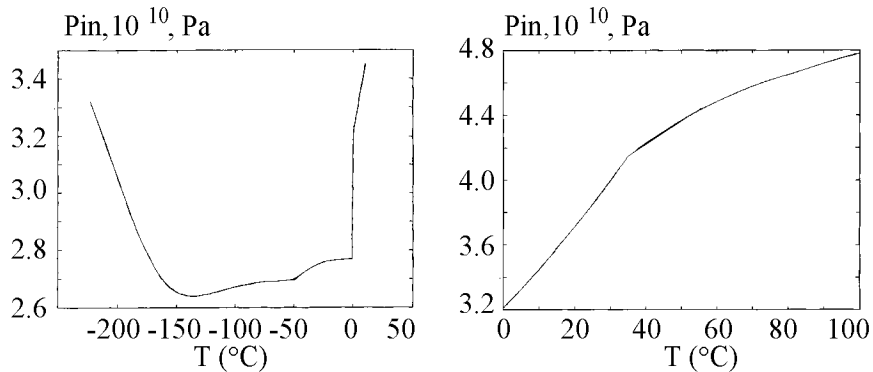


Fig. 1. (a) Theoretical temperature dependence of internal pressure (P_{in}) in ice including the point of [ice \leftrightarrow water] phase transition; (b) Theoretical temperature dependence of internal pressure (P_{in}) in water. Computer calculations were performed using eq. (7).

The minima of $P_{\text{in}}(T)$ for ice at -140^0 and -50^0 C in accordance with eq.(9) correspond to the most stable structure of this matter, related to temperature transition. In water some kind of transition appears at 35^0 C , near physiological temperature.

There may exist conditions when the derivatives of internal pressure P_{in} are equal to zero:

$$(a) : \left(\frac{\partial P_{\text{in}}}{\partial P_{\text{ext}}} \right)_T = 0 \quad \text{and} \quad (b) : \left(\frac{\partial P_{\text{in}}}{\partial T} \right)_{P_{\text{ext}}} = 0 \quad 9$$

This condition corresponds to the **minima of potential energy, i.e. to the most stable structure**

of given matter. In a general case there may be a few metastable states when conditions (9) are fulfilled.

Equation of state (7) may be useful for the study of mechanical properties of condensed matter and their change under different influences.

Differentiation of (6) by external pressure gives us at $T = \text{const}$:

$$V_{fr} + \frac{\partial P_{fr}}{\partial P_{ext}}(P_{ex} + P_{in}) + V_{fr} \frac{\partial P_{in}}{\partial P_{ext}} = \frac{\partial P_{ef}}{\partial P_{ext}} \quad 10$$

Dividing the left and right part of (10) by free volume V_{fr} we obtain:

$$\left(\frac{\partial P_{in}}{\partial P_{ext}} \right)_T = \left(\frac{\partial P_{ef}}{\partial P_{ext}} \right)_T - \left[1 + \beta_T(P_{ext} + P_{in}) \right]_T \quad 11$$

where: $\beta_T = -(\partial V_{fr}/\partial P_{ext})/V_{fr}$ is isothermal compressibility. From (9) and (11) we derive condition for the *maximum stability* of matter structure:

$$\left(\frac{\partial P_{ef}}{\partial P_{ext}} \right)_T = 1 + \beta_T^0 P_{tot}^{opt} \quad 12$$

where: $P_{tot}^{opt} = P_{ext} + P_{in}^{opt}$ is the "optimum" total pressure.

The derivative of (6) by temperature gives us at $P_{ext} = \text{const}$:

$$P_{tot} \left(\frac{\partial V_{fr}}{\partial T} \right)_{P_{ext}} + V_{fr} \left(\frac{\partial P_{in}}{\partial T} \right)_{P_{ext}} = \left(\frac{\partial U_{ef}}{\partial T} \right)_{P_{ext}} = C_V \quad 13$$

where

$$\left(\frac{\partial V_{fr}}{\partial T} \right)_{P_{ext}} = \left(\frac{\partial V_0}{\partial T} \right)_{P_{ext}} - \frac{4}{3} \pi N_0 \left(\frac{\partial \alpha^*}{\partial T} \right)_{P_{ext}} \quad 14$$

$$\text{and } \left(\frac{\partial V_{tot}}{\partial T} \right)_{P_{ext}} = \frac{\partial P_{in}}{\partial T} \quad 14a$$

From our mesoscopic theory of refraction index (Part 1 of [3]) the acting polarizability α^* is:

$$\alpha^* = \frac{\left(\frac{n^2-1}{n^2} \right)}{\frac{4}{3} \pi \frac{N_0}{V_0}} \quad 15$$

When condition (9b) is fulfilled, we obtain for optimum internal pressure (P_{in}^{opt}) from (13):

$$P_{in}^{opt} = C_V / \left(\frac{\partial V_{fr}}{\partial T} \right)_{P_{ext}} - P_{ext} \quad 16$$

or

$$P_{in}^{opt} = \frac{C}{V_{fr}\gamma} - P_{ext}, \quad 17$$

where

$$\gamma = (\partial V_{fr}/\partial T)/V_{fr} \quad 18$$

is the thermal expansion coefficient;

V_{fr} is the total free volume in 1 mole of condensed matter:

$$V_{fr} = V_0 - V_{exc} = V_0/n^2 \quad 19$$

It is taken into account in (13) and (19) that

$$(\partial V_{exc}/\partial T) \cong 0 \quad 20$$

because, as has been shown earlier (Fig.25a of [1] and Part 1 of [3]),

$$\partial \alpha^*/\partial T \cong 0$$

Dividing the left and right parts of (13) by $P_{tot} V_{fr} = U_{ef}$, we obtain for the heat expansion coefficient:

$$\gamma = \frac{C_V}{U_{ef}} - \frac{1}{P_{tot}} \left(\frac{\partial P_{in}}{\partial T} \right)_{P_{ext}} \quad 21$$

Under metastable states, when condition (9 b) is fulfilled,

$$\gamma^0 = C_V/U_{ef} \quad 22$$

Putting (8) into (12), we obtain for isothermal compressibility of metastable states corresponding to (9a) following formula:

$$\beta_T^0 = \frac{V_0 T_{kin}}{n^2 U_{tot}^2} \left(\frac{\partial U_{ef}}{\partial P_{ext}} - 1 \right) \quad 23$$

It seems that our equation of state (7) may be used to study different types of external influences (pressure, temperature, electromagnetic radiation, deformation, etc.) on the thermodynamic and mechanic properties of solids and liquids.

3. Vapor pressure

When a liquid is incubated long enough in a closed vessel at constant temperature, then an equilibrium between the liquid and vapor is attained.

At this moment, the number of molecules evaporated and condensed back to liquid is equal. The same is true of the process of sublimation.

There is still no satisfactory quantitative theory for *vapor pressure* calculation.

We can suggest such a theory using our notion of *superdeformons*, representing the biggest thermal fluctuations (see Table 1 and Introduction). The basic idea is that the external equilibrium vapor pressure is related to internal one (P_{in}^S) with coefficient determined by the probability of cavitation fluctuations (superdeformons) in the **surface layer** of liquids or solids.

In other words due to excitation of superdeformons with probability (P_D^S), the internal pressure (P_{in}^S) in surface layers, determined by the total contributions of all intramolecular interactions turns to external one - vapor pressure (P_V). It is something like a compressed spring energy realization due to trigger switching off.

For taking into account the difference between the surface and bulk internal pressure (P_{in}) we introduce the semiempirical surface pressure factor (q^S) as:

$$P_{in}^S = q^S P_{in} - P_{ext} = q^S \cdot \frac{n^2 U_{tot}}{V_0 S} - P_{ext} \quad 24$$

where: P_{in} corresponds to eq.(7); $S = T_{kin}/U_{tot}$ is a total structure factor.

The value of surface factor (q^S) for liquid and solid states is not the same:

$$q_{liq}^S < q_{sol}^S \quad 25$$

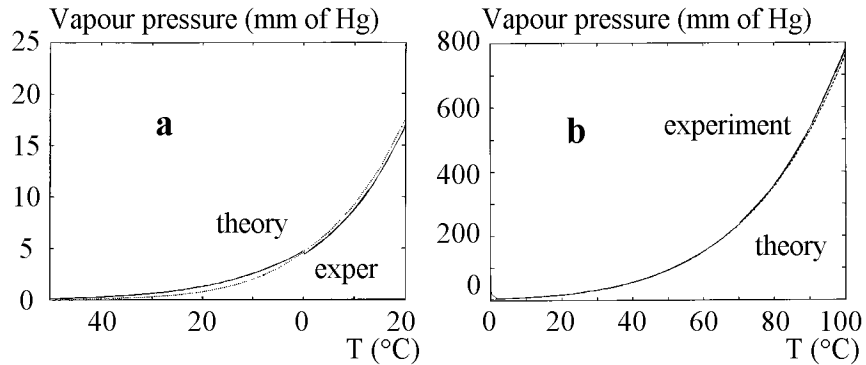


Fig. 2. a) Theoretical (—) and experimental (••) temperature dependences of vapor pressure (P_{vap}) for ice (a) and water (b) including phase transition region. Computer calculations were performed using eq. (26).

Multiplying (24) to probability of superdeformons excitation we obtain for vapor pressure, resulting from evaporation or sublimation, the following formulae:

$$P_{vap} = P_{in}^S \cdot P_D^S = \left(q^S \frac{n^2 U_{tot}^2}{V_0 T_{kin}} - P_{ext} \right) \cdot \exp\left(-\frac{E_D^S}{kT}\right) \quad 26$$

where:

$$P_D^S = \exp\left(-\frac{E_D^S}{kT}\right) \quad 27$$

is a probability of superdeformons excitation (see eqs. 3.37, 3.32 and 3.33).

We can assume, that the difference in the surface and bulk internal pressure is determined mainly by difference in total internal energy (U_{tot}) but not in kinetic one (T_k). Then a pressure surface factor could be presented as:

$$q^S = \gamma^2 = (U_{in}/U_{tot})^2$$

where: $\gamma = U_{tot}^S/U_{tot}$ is the **surface energy factor**, reflecting the ratio of surface and bulk total energy.

Theoretical calculated temperature dependences of vapor pressure, described by (26) coincide very well with experimental ones for water at $q_{liq}^S = 3.1$ ($\gamma_l = 1.76$) and for ice at $q_{sol}^S = 18$ ($\gamma_s = 4.24$) (Fig. 2).

The almost five-times difference between q_{sol}^S and q_{liq}^S means that the *surface* properties of ice differ from *bulk* ones much more than for liquid water.

The surface factors q_{liq}^S and q_{sol}^S should be considered as a fit parameters. The $q^S = \gamma^2$ is the only one fit parameter that was used in our hierarchic mesoscopic theory. Its calculation from the known vapor pressure or surface tension can give an important information itself.

4. Surface tension

The resulting surface tension is introduced in our mesoscopic model as a sum:

$$\sigma = (\sigma_{tr} + \sigma_{lb}) \quad 28$$

where: σ_{tr} and σ_{lb} are translational and librational contributions to surface tension. Each of these components can be expressed using our mesoscopic state equation (6, 7), taking into account the difference between surface and bulk total energies (q^S), introduced in previous section:

$$\sigma_{tr,lb} = \frac{1}{\pi (V_{ef})_{tr,lb}^{2/3}} \left[\frac{q^S P_{tot} (P_{ef} V_{ef})_{tr,lb} - P_{tot} (P_{ef} V_{ef})_{tr,lb}}{(P_{ef} + P_t)_{tr} + (P_{ef} + P_t)_{lb} + (P_{con} + P_{cMt})} \right] \quad 29$$

where $(V_{ef})_{tr,lb}$ are volumes of primary tr and lib effectons, related to their concentration $(n_{ef})_{tr,lb}$ as:

$$(V_{ef})_{tr,lb} = (1/n_{ef})_{tr,lb};$$

$$r_{tr,lb} = \frac{1}{\pi} (V_{ef})_{tr,lb}^{2/3}$$

is an effective radius of the primary translational and librational effectons, localized on the surface of condensed matter; q^S is the surface factor, equal to that used in eq.(24-26); $[P_{tot} = P_{in} + P_{ext}]$ is a total pressure, corresponding to eq.(6); $(P_{ef})_{tr,lb}$ is a total probability of primary effecton excitations in the (a) and (b) states:

$$(P_{ef})_{tr} = (P_{ef}^a + P_{ef}^b)_{tr}$$

$$(P_{ef})_{lb} = (P_{ef}^a + P_{ef}^b)_{lb}$$

$(P_t)_{tr}$ and $(P_t)_{lb}$ in (29) are the probabilities of corresponding transition excitation;

$P_{con} = P_{ac} + P_{bc}$ is the sum of probabilities of [a] and [b] *convertions*; $P_{cMt} = P_{ac} \cdot P_{bc}$ is the probability of Macroconvertion (see Introduction and Chapter 4).

The eq. (29) contains the ratio:

$$(V_{ef}/V_{ef}^{2/3})_{tr,lb} = l_{tr,lb} \quad 30$$

where: $l_{tr} = (1/n_{ef})_{tr}^{1/3}$ and $l_{lb} = (1/n_{ef})_{lb}^{1/3}$ are the length of the ribs of the primary translational and librational effectons, approximated by cube.

Using (30) and (29) the resulting surface tension (28) can be presented as:

$$\sigma = \sigma_{tr} + \sigma_{lb} = \pi \frac{P_{tot}(q^S - 1) \cdot \left[(P_{ef})_{tr}l_{tr} + (P_{ef})_{lb}l_{lb} \right]}{(P_{ef} + P_t)_{tr} + (P_{ef} + P_t)_{lb} + (P_{con} + P_{cMt})} \quad 31$$

where translational component of surface tension is:

$$\sigma_{tr} = \pi \frac{P_{tot}(q^S - 1)(P_{ef})_{tr}l_{tr}}{(P_{ef} + P_t)_{tr} + (P_{ef} + P_t)_{lb} + (P_{con} + P_{cMt})} \quad 32$$

and librational component of σ is:

$$\sigma_{lb} = \pi \frac{P_{tot}(q^S - 1)(P_{ef})_{lb}l_{lb}}{(P_{ef} + P_t)_{tr} + (P_{ef} + P_t)_{lb} + (P_{con} + P_{cMt})} \quad 33$$

Under the boiling condition when $q^S \rightarrow 1$ as a result of ($U_{tot}^S \rightarrow U_{tot}$), then σ_{tr} , σ_{lb} and σ tends to zero. The maximum depth of the surface layer, which determines the σ_{lb} is equal to the length of edge of cube (l_{lb}), that approximates the shape of primary **librational** effectons. It decreases from about 20 Å at 0°C till about 2.5 Å at 100°C (see Fig. 7b of [1] or Fig. 4b of [2]). Monotonic decrease of (l_{lb}) with temperature could be accompanied by nonmonotonic change of probabilities of [lb/tr] convertions and macroconvertions excitations (see comments to Fig. 7a of [1] or to Fig 4a of [2]). Consequently, the temperature dependence of surface tension on temperature can display anomalies at definite temperatures. This consequence of our theory is confirmed experimentally (Adamson, 1982; Drost-Hansen and Lin Singleton, 1992).

The thickness of layer (l_{tr}), responsible for contribution of **translational** effectons in surface tension (σ_{tr}) has the dimension of one molecule in all temperature interval for liquid water.

The results of computer calculations of σ (eq.31) for water and experimental data are presented at Fig.3.

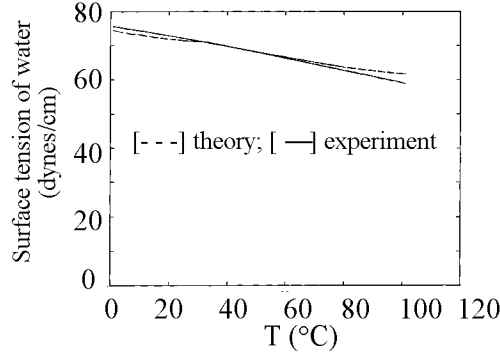


Fig. 3. Experimental (—) and theoretical (---) temperature dependences of the surface tension for water, calculated from eq.(31).

It is obvious, that the correspondence between theory and experiment is very good, confirming in such a way the correctness of our model and Hierarchic concept in general.

5. Mesoscopic theory of thermal conductivity

Thermal conductivity may be related to phonons, photons, free electrons, holes and

[electron-hole] pairs movement.

We will discuss here only the main type of thermal conductivity in condensed matter, related to phonons.

The analogy with the known formula for thermal conductivity (κ) in the framework of the kinetic theory for gas is used [4]:

$$\kappa = \frac{1}{3} C_v v_s \Lambda \quad 34$$

where C_v is the heat capacity of condensed matter, v_s is sound velocity, characterizing the speed of phonon propagation in matter, and Λ is the average **length of free run** of phonons.

The value of Λ depends on the scattering and dissipation of phonons at other phonons and different types of defects. Usually decreasing temperature increases Λ .

Different factors influencing a thermal equilibrium in the system of phonons are discussed. Among them are the so called U- and N- processes describing the types of phonon-phonon interaction. However, the traditional theories are unable to calculate Λ directly.

Mesoscopic theory introduce two contributions to thermal conductivity: related to phonons, irradiated by secondary effectons and forming **secondary** translational and librational deformons ($\kappa_{sd})_{tr,lb}$ and to phonons, irradiated by a and b convertons [tr/lb], forming the convertons-induced deformons ($\kappa_{cd})_{ac,bc}$:

$$\kappa = (\kappa_{sd})_{tr,lb} + (\kappa_{cd})_{ac,bc} = \frac{1}{3} C_v v_s [(\Lambda_{sd})_{tr,lb} + (\Lambda_{cd})_{ac,bc}] \quad 35$$

where: **free runs** of secondary phonons (tr and lb) are represented as:

$$1/(\Lambda_{sd})_{tr,lb} = 1/(\Lambda_{tr}) + 1/(\Lambda_{lb}) = (\bar{v}_d)_{tr}/v_s + (\bar{v}_d)_{lb}/v_s$$

consequently:

$$1/(\Lambda_{sd})_{tr,lb} = \frac{v_s}{(\bar{v}_d)_{tr} + (\bar{v}_d)_{lb}} \quad 36$$

and free runs of convertons-induced phonons:

$$1/(\Lambda_{cd})_{ac,bc} = 1/(\Lambda_{ac}) + 1/(\Lambda_{bc}) = (v_{ac})/v_s + (v_{bc})/v_s$$

$$\text{consequently: } (\Lambda_{sd})_{tr,lb} = \frac{v_s}{(v_d)_{tr} + (v_d)_{lb}} \quad 37$$

The heat capacity: $C_V = \partial U_{tot}/\partial T$ can be calculated also from our theory (see Chapter 4 and 5).

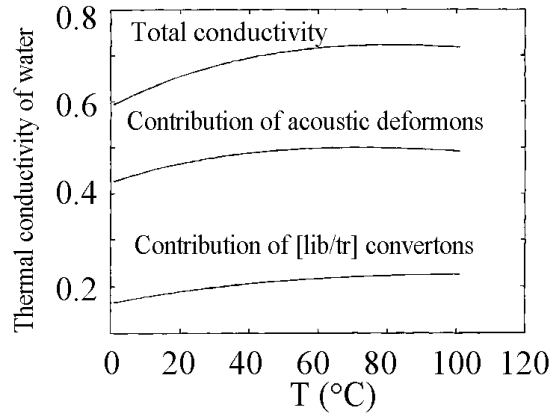


Fig. 4. Temperature dependences of total thermal conductivity for water and contributions, related to acoustic deformons and [lb/tr]convertons. The dependences were calculated, using eq. (37).

Quantitative calculations show that formula (35), based on our mesoscopic model, works well for water (Fig. 4). **It could be used for any other condensed matter also if positions of**

translational and librational bands, sound velocity and molar volume for this matter at the same temperature interval are known.

The small difference between experimental and theoretical data can reflect the contributions of non-phonon process in thermal conductivity, related to macrodeformons, superdeformons and macroconvertons, i.e. big fluctuations.

6. Mesoscopic theory of viscosity for liquids and solids

The **viscosity** is determined by the energy dissipation as a result of medium (liquid or solid) structure deformation. Viscosity corresponding to the shift deformation is named *shear viscosity*. So-called *bulk viscosity* is related to deformation of volume parameters and corresponding dissipation. These types of viscosity have not the same values and nature.

The statistical theory of irreversible process leads to the following expression for shear viscosity (Prokhorov, 1988):

$$\eta = nkT\tau_p + (\mu_\infty - nkT)\tau_q \quad 38$$

where n is the concentration of particles, μ_∞ is the modulus of instant shift characterizing the instant elastic reaction of medium, τ_p and τ_q are the relaxation times of impulses and coordinates, respectively.

However, eq.(38) is inconvenient for practical purposes due to difficulties in determination of τ_p , τ_q and μ_∞ .

Sometimes in a narrow temperature interval the empiric Ondrade equation is working:

$$\eta = A(T) \cdot \exp(\beta/T) \quad 39$$

$A(T)$ is a function poorly dependent on temperature.

A good results in study the microviscosity problem were obtained by combining the model of molecular rotational relaxation [5] and the Kramers equation (Åkesson et al., 1991). However, the using of the fit parameters was necessarily in this case also.

We present here our mesoscopic theory of viscosity. To this end the dissipation processes, related to $(A \rightleftharpoons B)_{tr,lb}$ cycles of translational and librational macroeffectons and (a,b)-*convertons* excitations were used. The same approach was employed for elaboration of mesoscopic theory of diffusion in condensed matter (see next section).

In contrast to liquid state, the viscosity of solids is determined by the biggest fluctuations: **supereffectons** and **superdeformons**, resulting from simultaneous excitations of translational and librational macroeffectons and macrodeformons in the same volume.

The dissipation phenomena and ability of particles or molecules to diffusion are related to the local fluctuations of the free volume $(\Delta v_f)_{tr,lb}$. According to mesoscopic theory, the fluctuations of free volume and that of density occur in the almost macroscopic volumes of translational and librational macrodeformons and in mesoscopic volumes of **macroconvertons**, equal to volume of primary librational effecton at the given conditions. Translational and librational types of macroeffectons determine two types of viscosity, i.e. translational (η_{tr}) and librational (η_{lb}) ones. They can be attributed to the bulk viscosity. The contribution to viscosity, determined by (a and b)-*convertons* is much more local and may be responsible for microviscosity and mesoviscosity.

Let us start from calculation of the additional free volumes (Δv_f) originating from fluctuations of density, accompanied the translational and librational macrodeformons (macrotransitions).

For 1 mole of condensed matter the following ratio between free volume and concentration fluctuations is true:

$$\left(\frac{\Delta v_f}{v_f} \right)_{tr,lb} = \left(\frac{\Delta N_0}{N_0} \right)_{tr,lb} \quad 40$$

where N_0 is the average number of molecules in 1 mole of matter

$$\text{and } (\Delta N_0)_{tr,lb} = N_0 \left(\frac{P_D^M}{Z} \right)_{tr,lb} \quad 41$$

is the number of molecules changing their concentration as a result of translational and librational macrodeformons excitation.

The probability of translational and librational macroeffectons excitation (see eqs. 3.23; 3.24):

$$\left(\frac{P_D^M}{Z} \right)_{tr,lb} = \frac{1}{Z} \exp \left(-\frac{\epsilon_D^M}{kT} \right)_{tr,lb} \quad 42$$

where Z is the total partition function of the system (Chapter 4 of [1, 2]).

Putting (41) to (40) and dividing to Avogadro number (N_0), we obtain the fluctuating free volume, reduced to 1 molecule of matter:

$$\Delta v_f^0 = \frac{\Delta v_f}{N_0} = \left[\frac{v_f}{N_0} \left(\frac{P_D^M}{Z} \right) \right]_{tr,lb} \quad 43$$

It has been shown above (eq.19) that the average value of free volume in 1 mole of matter is:

$$v_f = V_0/n^2$$

Consequently, for reduced fluctuating (additional) volume we have:

$$(\Delta v_f^0)_{tr,lb} = \frac{V_0}{N_0 n^2} \frac{1}{Z} \exp \left(-\frac{\epsilon_D^M}{kT} \right)_{tr,lb} \quad 44$$

Taking into account the dimensions of viscosity and its physical sense, it should be proportional to the work (activation energy) of fluctuation-dissipation, necessary for creating the unit of additional free volume: $(E_D^M/\Delta v_f^0)$, and the period of $(A \rightleftharpoons B)_{tr,lb}$ cycles of translational and librational macroeffectons $\tau_{A \rightleftharpoons B}$, determined by the life-times of all intermediate states (eq.46).

In turn, the energy of dissipation should be strongly dependent on the structural factor (S): the ratio of kinetic energy of matter to its total internal energy. We assume here that this dependence for viscosity calculation is cubical: $(T_k/U_{tot})^3 = S^3$.

Consequently, the contributions of translational and librational macrodeformons to resulting viscosity we present in the following way:

$$\eta_{tr,lb}^M = \left[\frac{E_D^M}{\Delta v_f^0} \cdot \tau^M \left(\frac{T_k}{U_{tot}} \right)^3 \right]_{tr,lb} \quad 45$$

where: reduced fluctuating volume (Δv_f^0) corresponds to (44); the energy of macrodeformons: $[E_D^M = -kT \cdot (\ln P_D^M)]_{tr,lb}$.

The cycle-periods of the *tr* and *lib* macroeffectons has been introduced as:

$$[\tau^M = \tau_A + \tau_B + \tau_D]_{tr,lb} \quad 46$$

where: characteristic life-times of macroeffectons in A, B-states and that of transition state in the volume of primary electromagnetic deformons can be presented, correspondingly, as follows:

$$[\tau_A = (\tau_a \cdot \tau_{\bar{a}})^{1/2}]_{tr,lb} \quad \text{and} \quad [\tau_B = (\tau_b \cdot \tau_{\bar{b}})^{1/2}]_{tr,lb} \quad 47$$

$$[\tau_D = |(1/\tau_A) - (1/\tau_B)|^{-1}]_{tr,lb}$$

Using (47, 46 and 44) it is possible to calculate the contributions of $(A \rightleftharpoons B)$ cycles of translational and librational macroeffectons to viscosity separately, using (45).

The averaged contribution of macroexcitations (*tr* and *lb*) in viscosity is:

$$\eta^M = \left[(\eta)_{tr}^M \cdot (\eta)_{lb}^M \right]^{1/2} \quad 48$$

The contribution of *a* and *b convertons* to viscosity of liquids could be presented in a similar to (44-48) manner after substituting the parameters of *tr* and *lb* macroeffectons with parameters of *a* and *b* convertons:

$$\eta_{ac,bc} = \left[\frac{E_c}{\Delta v_f^0} \tau_c \left(\frac{T_k}{U_{tot}} \right)^3 \right]_{ac,bc} \quad 49$$

where: reduced fluctuating volume of (*a* and *b*) convertons $(\Delta v_f^0)_{ac,bc}$ corresponds to:

$$(\Delta v_f^0)_{ac,bc} = \frac{V_0}{N_0 n^2} \frac{1}{Z} P_{ac,bc} \quad 50$$

where: P_{ac} and P_{bc} are the relative probabilities of *tr/lib* interconversions between *a* and *b* states of translational and librational primary effectons (see Introduction and Chapter 4); E_{ac} and E_{bc} are the excitation energies of (*a* and *b*) convertons correspondingly (see Chapter 4 of [1] and [2]);

Characteristic life-times for *ac*-convertons and *bc*-convertons [*tr/lib*] in the volume of primary librational effectons ("flickering clusters") could be presented as:

$$\begin{aligned} \tau_{ac} &= (\tau_a)_{tr} + (\tau_a)_{lb} = (1/v_a)_{tr} + (1/v_a)_{lb} \\ \tau_{bc} &= (\tau_b)_{tr} + (\tau_b)_{lb} = (1/v_b)_{tr} + (1/v_b)_{lb} \end{aligned} \quad 51$$

The averaged contribution of the both types of convertons in viscosity is:

$$\eta_c = (\eta_{ac} \cdot \eta_{bc})^{1/2} \quad 52$$

This contribution could be responsible for microviscosity or better term: **mesoviscosity**, related to volumes, equal to that of primary librational effectons.

The resulting viscosity (Fig.5) is a sum of the averaged contributions of macrodeformons and convertons:

$$\eta = \eta^M + \eta_c \quad 53$$

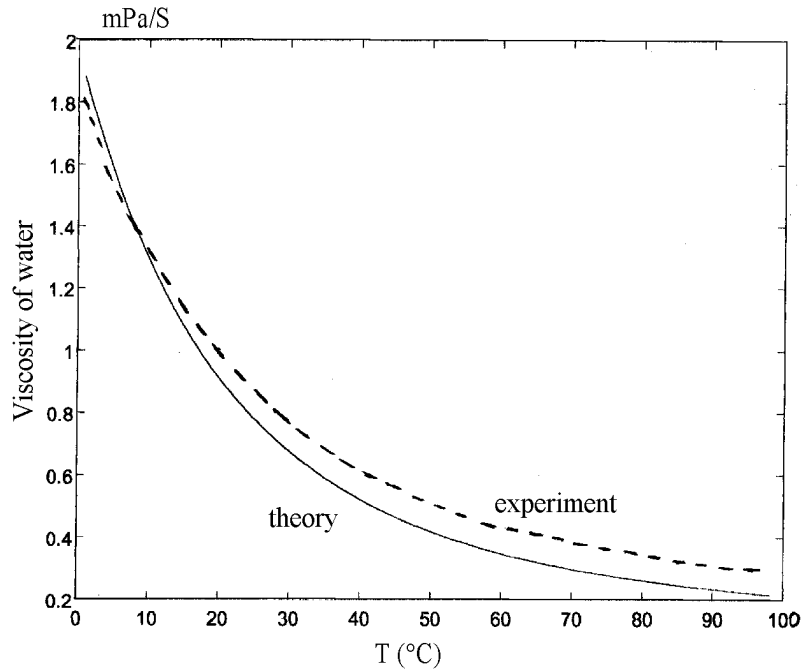


Fig. 5. Theoretical and experimental temperature dependences of viscosities for water. Computer calculations were performed using eqs. (44 - 53) and (4.3; 4.36).

The best correlation between theoretical and experimental data was achieved after assuming that only $(\pi/2 = 2\pi/4)$ part of the period of above described fluctuation cycles is important for dissipation and viscosity. Introducing this factor to equations for viscosity calculations gives up very good correspondence between theory and experiment in all temperature interval (0-100°C) for

water (Fig.5).

As will be shown below the same factor, introducing the effective time of fluctuations $[\frac{\tau}{\pi/2}]$, leads to best results for self-diffusion coefficient calculation.

In the classical hydrodynamic theory the sound absorption coefficient (α) obtained by Stokes includes share (η) and bulk (η_b) averaged macroviscosities:

$$\alpha = \frac{\Omega}{2\rho v_s^3} \left(\frac{4}{3}\eta + \eta_b \right), \quad 54$$

where Ω is the angular frequency of sound waves; ρ is the density of liquid.

Bulk viscosity (η_b) is usually calculated from the experimental η and α . It is known that for water:

$$(\eta_b/\eta) \sim 3.$$

The viscosity of solids

In accordance with our model, the biggest fluctuations: *supereffectons and superdeformons* (see Introduction) are responsible for viscosity and diffusion phenomena in solid state. Superdeformons are accompanied by the emergency of cavitation fluctuations in liquids and the defects in solids. The presentation of viscosity formula in solids (η_s) is similar to that for liquids:

$$\eta_s = \frac{E_s}{(\Delta v_f^0)_s} \cdot \tau_s \left[\frac{T_k}{U_{tot}} \right]^3 \quad 55$$

where: reduced fluctuating volume, related to superdeformons excitation $(\Delta v_f^0)_s$ is:

$$(\Delta v_f^0)_s = \frac{V_0}{N_0 n^2} \frac{1}{Z} P_s \quad 56$$

where: $P_s = (P_D^M)_{tr} \cdot (P_D^M)_{lb}$ is the relative probability of superdeformons, equal to product of probabilities of *tr* and *lb* macrodeformons excitation (see 42); $E_s = -kT \cdot \ln P_s$ is the energy of superdeformons (see Chapter 4);

Characteristic cycle-period of ($A^* \rightleftharpoons B^*$) transition of supereffectons is related to its life-times in A^* , B^* and transition D^* states (see eq.46) as was shown in section 4.3:

$$\tau_s = \tau_{A^*} + \tau_{B^*} + \tau_{D^*} \quad 56a$$

The viscosity of ice, calculated from eq.(55) is bigger than that of water (eq.53) to about 10^5 times. This result is in accordance with available experimental data.

7. Brownian diffusion

The important formula obtained by Einstein in his theory of Brownian motion is for translational motion of particle:

$$r^2 = 6Dt = \frac{kT}{\pi\eta a} t \quad 57$$

and that for rotational Brownian motion:

$$\varphi^2 = \frac{kT}{4\pi\eta a^3} t \quad 58$$

where: a - radius of spherical particle, much larger than dimension of molecules of liquid. The coefficient of diffusion D for Brownian motion is equal to:

$$D = \frac{kT}{6\pi\eta a} \quad 59$$

If we take the angle $\bar{\varphi}^2 = 1/3$ in (59), then the corresponding rotational correlation time comes to the form of the known Stokes- Einstein equation:

$$\tau = \frac{4}{3} \pi a^3 \frac{1}{k} \left(\frac{\eta}{T} \right) \quad 60$$

All these formulas (57 - 60) include macroscopic share viscosity (η) corresponding to our (53).

8. Self-diffusion in liquids and solids

Molecular theory of self-diffusion, as well as general concept of *transfer phenomena* in condensed matter is extremely important, but still unresolved problem.

Simple semiempirical approach developed by Frenkel leads to following expression for diffusion coefficient in liquid and solid:

$$D = \frac{a^2}{\tau_0} \exp(-W/kT) \quad 61$$

where [a] is the distance of fluctuation jump; $\tau_0 \sim (10^{-12} \div 10^{-13})s$ is the average period of molecule oscillations between jumps; W - activation energy of jump.

The parameters: a, τ_0 and W should be considered as a fit parameters.

In accordance with **mesoscopic theory**, the process of **self-diffusion** in liquids, like that of **viscosity**, described above, is determined by two contributions:

a) the **collective, nonlocal contribution**, related to translational and librational macrodeformons ($D_{tr,lb}$);

b) the **local contribution**, related to coherent clusters flickering: [dissociation/association] of primary librational effectons (*a* and *b*)- convertons ($D_{ac,bc}$).

Each component of the resulting coefficient of self-diffusion (D) in liquid could be presented as the ratio of fluctuation volume cross-section surface: $[\Delta v_f^0]^{2/3}$ to the period of macrofluctuation (τ). The first contribution to coefficient **D**, produced by translational and librational macrodeformons is:

$$D_{tr,lb} = \left[(\Delta v_f^0)^{2/3} \cdot \frac{1}{\tau^M} \right]_{tr,lb} \quad 62$$

where: the surface cross-sections of reduced fluctuating free volumes (see eq.43) fluctuations in composition of macrodeformons (*tr* and *lb*) are:

$$(\Delta v_f^0)_{tr,lb}^{2/3} = \left[\frac{V_0}{N_0 n^2} \frac{1}{Z} \exp\left(-\frac{\epsilon_D^M}{kT}\right) \right]_{tr,lb}^{2/3} \quad 63$$

$(\tau^M)_{tr,lb}$ are the characteristic (*A* \leftrightarrow *B*) cycle-periods of translational and librational macroeffectons (see eqs. 46 and 47).

The averaged component of self-diffusion coefficient, which takes into account both types of nonlocal fluctuations, related to translational and librational macroeffectons and macrodeformons, can be find as:

$$D^M = [(D)_{tr}^M \cdot (D)_{lb}^M]^{1/2} \quad 64$$

The formulae for the second, local contribution to self-diffusion in liquids, related to (*a* and *b*) convertons ($D_{ac,bc}$) are symmetrical by form to that, presented above for nonlocal processes:

$$D_{ac,bc} = \left[(\Delta v_f^0)^{2/3} \cdot \frac{1}{\tau_s} \right]_{ac,bc} \quad 65$$

where: reduced fluctuating free volume of (*a* and *b*) convertons $(\Delta v_f^0)_{ac,bc}$ is the same as was used above in mesoscopic theory of viscosity (eq.50):

$$(\Delta v_f^0)_{ac,bc} = \frac{V_0}{N_0 n^2} \frac{1}{Z} P_{ac,bc} \quad 66$$

where: P_{ac} and P_{bc} are the relative probabilities of *tr/lib* interconversions between *a* and *b* states of translational and librational primary effectons (see Introduction and Chapter 4)

The averaged local component of self-diffusion coefficient, which takes into account both types of convertons (*ac* and *bc*) is:

$$D_C = [(D)_{ac} \cdot (D)_{bc}]^{1/2} \quad 67$$

In similar way we should take into account the contribution of macroconvertions (D_{Mc}):

$$D_{Mc} = \left(\frac{V_0}{N_0 n^2} \frac{1}{Z} P_{Mc} \right)^{2/3} \cdot \frac{1}{\tau_{Mc}} \quad 67a$$

where: $P_{Mc} = P_{ac} \cdot P_{bc}$ is a probability of macroconvertion excitation;

the life-time of macroconvertion is:

$$\tau_{Mc} = (\tau_{ac} \cdot \tau_{bc})^{1/2} \quad 67b$$

The cycle-period of (ac) and (bc) convertions are determined by the sum of life-times of intermediate states of primary translational and librational effectons:

$$\tau_{ac} = (\tau_a)_{tr} + (\tau_a)_{lb}; \quad \text{and} \quad \tau_{bc} = (\tau_b)_{tr} + (\tau_b)_{lb} \quad 67c$$

The life-times of primary and secondary effectons (lb and tr) in a - and b -states are the reciprocal values of corresponding state frequencies:

$$[\tau_a = 1/\nu_a; \tau_{\bar{a}} = 1/\nu_{\bar{a}}; \text{and} \tau_b = 1/\nu_b; \tau_{\bar{b}} = 1/\nu_{\bar{b}}]_{tr,lb} \quad 67d$$

$[\nu_a \text{ and } \nu_b]_{tr,lb}$ correspond to eqs. 4.8 and 4.9; $[\nu_{\bar{a}} \text{ and } \nu_{\bar{b}}]_{tr,lb}$ could be calculated using eqs.2.54 and 2.55.

The resulting coefficient of self-diffusion in liquids (D) is a sum of nonlocal (D^M) and local (D_c , D_{Mc}) effects contributions (see eqs.64 and 67):

$$D = D^M + D_c + D_{Mc} \quad 68$$

The effective fluctuation-times were taken the same as in previous section for viscosity calculation, using the correction factor $[(\pi/2) \cdot \tau]$.

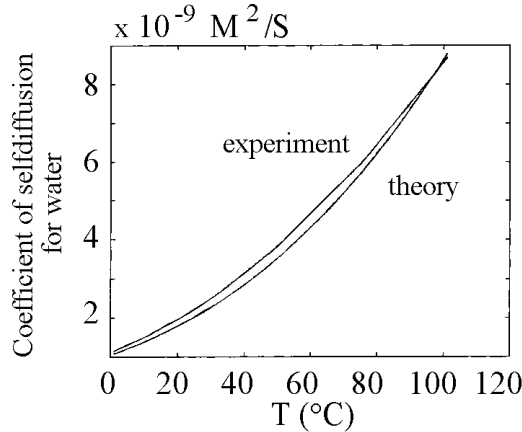


Fig. 6. Theoretical and experimental temperature dependences of self-diffusion coefficients in water. Theoretical coefficient was calculated using eq. 68.

Like in the cases of thermal conductivity, viscosity and vapor pressure, the results of theoretical calculations of self-diffusion coefficient coincide well with experimental data for water (Fig. 6) in temperature interval (0 – 100°C).

The self-diffusion in solids

In solid state only the biggest fluctuations: *superdeformons*, representing simultaneous excitation of translational and librational macrodeformons in the same volumes of matter are responsible for diffusion and the viscosity phenomena. They are related to origination and migration of the defects in solids. The formal presentation of superdeformons contribution to

self-diffusion in solids (D_s) is similar to that of macrodeformons for liquids:

$$D_s = (\Delta v_f^0)_s^{2/3} \cdot \frac{1}{\tau_s} \quad 69$$

where: reduced fluctuating free volume in composition of superdeformons $(\Delta v_f^0)_s$ is the same as was used above in mesoscopic theory of viscosity (eq.56):

$$(\Delta v_f^0)_s = \frac{V_0}{N_0 n^2} \frac{1}{Z} P_s \quad 70$$

where: $P_s = (P_D^M)_{tr} \cdot (P_D^M)_{lb}$ is the relative probability of superdeformons, equal to product of probabilities of *tr* and *lb* macrodeformons excitation (see 42).

Characteristic cycle-period of supereffectons is related to that of *tr* and *lb* macroeffectons like it was presented in eq.(56a):

$$\tau_s = \tau_{A^*} + \tau_{B^*} + \tau_{D^*} \quad 71$$

The self-diffusion coefficient for ice, calculated from eq.69 is less than that of water (eq.53) to about 10^5 times. This result is in accordance with available experimental data.

Strong decreasing of D in a course of phase transition: [water → ice] predicted by our mesoscopic theory also is in accordance with experiment (Fig. 7).

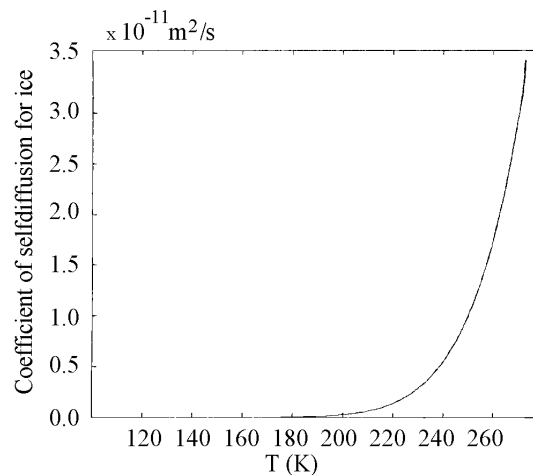


Fig. 7. Theoretical temperature dependences of self-diffusion coefficients in ice.

All these results allow to consider our mesoscopic theory of transfer phenomena as a quantitatively confirmed one. They point that the "mesoscopic bridge" between Micro- and Macro Worlds is wide and reliable indeed. It gives a new possibilities for understanding and detailed description of very different phenomena in solids and liquids.

One of the important consequences of our theory of viscosity and diffusion is the possibility of explaining numerous nonmonotonic temperature changes, registered by a number of physicochemical methods in various aqueous systems during the study of temperature dependences ([6], [7], [8], [9]; [10]; [11], [12]).

Most of them are related to diffusion or viscosity processes and may be explained by nonmonotonic changes of the refraction index, included in our equations: 44, 45, 50 for viscosity and eqs. 69, 70 for self-diffusion. For water these temperature anomalies of refraction index were revealed experimentally, using few wave lengths in the temperature interval 3 – 95° [13]. They are close to Drost-Hansen temperatures. The explanation of these effects, related to periodic variation of primary librational effectons stability with monotonic temperature change was presented as comments to Fig. 7a of [1] or Fig.4a of [2].

Another consequence of our theory is the elucidation of a big difference between librational η_{lb} (48), translational η_{tr} (45) viscosities and mesoviscosity, determined by [lb/tr] convertions (49 and 52).

The effect of mesoviscosity can be checked as long as the volume of a Brownian particle does not exceed much the volume of primary librational effectons (eq. 15). If we take a Brownian particle, much bigger than the librational primary effecton, then its motion will reflect only averaged share viscosity (eq.53).

The third consequence of the mesoscopic theory of viscosity is the prediction of nonmonotonic temperature behavior of the sound absorption coefficient α (51). Its temperature dependence must have anomalies in the same regions, where the refraction index has.

The experimentally revealed temperature anomalies of (n) also follow from our theory as a result of nonmonotonic $(a \Leftrightarrow b)_{lb}$ equilibrium behavior, stability of primary lb effectons and probability of [lb/tr] convertions excitation (see Discussion to Fig.7a of [1] or to Fig.4a of [2]).

Our model predicts also that in the course of transition from the laminar type of flow to the turbulent one the share viscosity (η) will increase due to increasing of structural factor (T_k/U_{tot}) in eq. 45.

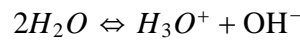
The superfluidity ($\eta \rightarrow 0$) in the liquid helium could be a result of inability of this liquid at the very low temperature for translational and librational macroeffectons excitations, i.e. $\tau^M \rightarrow 0$.

In turn, it is a consequence of tending to zero the life-times of secondary effectons and deformons in eqs.(45), responsible for dissipation processes, due to their Bose-condensation and transformation to primary ones (see Chapter 12 of [1]). The polyeffectons, stabilized by Josephson's junctions between primary effectons form the superfluid component of liquid helium.

9. Mesoscopic approach to proton conductivity in water, ice and other systems, containing hydrogen bonds

The numerous models of proton transitions in water and ice are usually related to migration of two types of defects in the ideal Bernal-Fowler structure [14]:

1. Ionic defects originated as a result of $2H_2O$ dissociation to hydroxonium and hydroxyl ions:



2. Orientational Bjerrum defects are subdivided to D (dopplet) and L (leer) ones.

D-defect (positive) corresponds to situation, when 2 protons are placed between two oxygen atoms, instead of the normal structure of hydrogen bond: $O \dots H - O$ containing 1 proton.

L-defect (negative) corresponds to opposite anomaly, when even 1 proton between two oxygens is absent. Reorientation of dipole moment of H_2O in the case of D- and L-defects leads to origination of charges:

$$q_B = q_D^+ = |q_L^-| = 0.38e \quad 72$$

The interrelation between the charge of electron (e), Bjerrum charge (q_B) and ionic charge (e_I) (Onsager, Dupius, 1962) is:

The general approach to problem of proton transition takes into account both types of defects: ionic and orientational. It was assumed that orientational defects originate and annihilate in the process of continuous migration of ions H^+ and OH^- through the water medium. Krjachko (1987) considers DL-pairs as a cooperative water cluster with linear dimensions of about 15\AA and with "kink". The Bjerrum's DL-pair is a limit case of such model.

The protons conductivity in water must decrease with temperature increasing due to decreasing and disordering of water clusters and chains.

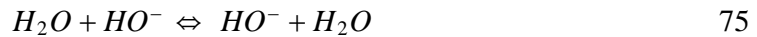
The *kink-soliton* model of orientational defects migration along the H_2O chain was developed by Sergienko (1986). Mobility of ionic defects exceeds the orientational ones about 10 times.

But it is important to point out that the strong experimental evidence confirming the existence of just Bjerrum type orientational defects are still absent.

Our mesoscopic model of proton diffusion in ice, water and other hydrogen bonds containing systems includes following stages:

1. Ionization of water molecules in composition of superdeformons and ionic defects origination;
2. Bordering by H_3^+O and HO^- the opposite surface-sides of primary librational effectons;
3. Tunneling of proton through the volume of primary effecton as a coherent water cluster (Bose-particle);
4. Diffusion of ions H_3^+O and HO^- in the less ordered medium between primary effectons can be realized in accordance with fluctuation mechanism described above in Section 8. The velocity of this stage is less than tunneling.

Transitions of protons and hydroxyl groups can occur also due to exchange processes (Antonchenko, 1991) like:



The rate of ions transferring due to exchange is about 10 times more, than diffusion velocity, but slower than that, determined by tunneling jumps.

5. The orientational defects can originate as a result of H_2O molecules rearrangements and conversions between translational and librational effectons in composition of superdeformons. Activation energy of superdeformons and macroconvertons in water is 10.2 kcal/M and about 12 kcal/M in ice (see 6.12; 6.13). The additional activation energy about 2-3 kcal/M is necessary for subsequent reorientation of surrounding molecules (Bjerrum, 1951).

Like the ionic defects, positive (D) and negative (L) defects can form a separated pairs on the opposite sides of primary effectons, approximated by parallelepiped. Such pairs means the effectons polarization.

Probability of H^+ or HO^- tunneling through the coherent cluster - primary effecton in the (a)-state is higher than that in the (b)-state as far (see 1.30-1.32 of [1]):

$$[E_a = T_{\text{kin}}^a + V_a] < [E_b = T_{\text{kin}}^b + V_b] \quad 76$$

where: $T_{\text{kin}}^a = T_{\text{kin}}^b$ are the kinetic energies of (a) and (b) states; $E_b - E_a = V_b - V_a$. is the difference between total and potential energies of these states.

In accordance with known theory of tunneling, the probability of passing the particle with mass (m) through the barrier with wideness (a) and height (ϵ) has a following dependence on these parameters:

$$|\psi_a| \sim \exp\left(-\frac{a}{b}\right) = \exp\left(-\frac{a(2m\epsilon)^{1/2}}{\hbar}\right) \quad 77$$

where:

$$b = \hbar/(2m\epsilon)^{1/2} \quad 78$$

is the effective wave function fading length.

Parameter (b) is similar to wave B most probable amplitude (A_B) with total energy $E_B = \epsilon$ (see eq. 2.22 of [1]):

$$b = A_B = \hbar/(2mE_B)^{1/2} \quad 79$$

With temperature decreasing the ($a \leftrightarrow b$)_{tr,lb} equilibrium of primary effectons shifts to the left:

$$K_{a \leftrightarrow b} = (P_a/P_b) \rightarrow \infty \quad 80$$

where $P_a \rightarrow 1$ and $P_b \rightarrow 0$ are the thermoaccessibilities of (a) and (b) states of primary effectons (see eqs. 4.10-4.12). The linear dimensions of primary effectons of ice also tend to infinity at $T \rightarrow 0$.

In water the tunneling stage of proton conductivity can be related to primary librational effectons only and their role increase with temperature decreasing. Dimensions of translational effectons in water does not exceed that of one molecule as it leads from our computer calculations.

Increasing of protons conductivity in ice with respect to water, in accordance with our model, is a consequence of participation of translational primary effectons in tunneling of $[H^+]$ besides librational ones, as well as significant elevation of primary librational effectons dimensions. Increasing of the total contribution of tunneling process in protons migration in ice rise up their resulting transferring velocity comparing to water.

The external electric field induce:

a) redistribution of positive and negative charges on the surface of primary effectons determined by ionic defects and corresponding orientational defects;

b) orientation of polarized primary effectons in field, making quasi-continuous polyeffectons chains and that of the effectons orchestrated superclusters.

These effects create the conditions for relay mechanism of $[H^+]$ and H_3^+O transmitting in the direction of electric field and $[HO^-]$ in the opposite one.

In accordance with our hierarchic model, the $[H^+]$ transition mechanism includes the alternation of tunneling, exchange and usual diffusion processes.

10. Regulation of pH and shining of water by electromagnetic and acoustic fields

In accordance with our model, water dissociation reaction:



leading to *increase of protons concentration* is dependent on probability of $[A_S^* \rightarrow B_S^*]$ transitions in supereffectons. This means that stimulation of $[A_S^* \rightarrow B_S^*]$ transitions (superdeformons) by **ultrasound** with resonant frequencies, corresponding to frequency of these transitions, should lead to decreasing of pH, i.e. to increasing the concentration of protons $[H^+]$.

The $[A_S \rightarrow B_S]$ transitions of supereffectons can be accompanied by origination of **cavitation fluctuations** (cavitation microbubbles). The opposite $[B_S \rightarrow A_S]$ transitions are related to the collapse of these microbubbles. As a result of this adiabatic process, water vapor in the bubbles is heated up to 4000 – 6000⁰ K. The usual energy of superdeformons in

water (Section 6.3):

$$\epsilon_D^S = 10.2 \text{ kcal/M} \simeq RT^* \quad 81$$

correspond to local temperature $T^* \simeq 5000 \text{ }^0\text{K}$. For the other hand it is known, that even $2000 \text{ }^0\text{K}$ is enough already for partial dissociation of water molecules inside bubbles (about 0.01% of total amount of bubble water).

The variable pressure (P), generated by ultrasound in liquid is dependent on its intensity (I , wt/cm^2) like:

$$P = (\rho v_s I)^{1/2} \cdot 4.6 \cdot 10^{-3} (\text{atm}) \quad 82$$

where ρ is density of liquid; v_s - sound velocity (m/s).

$[A_S^* \rightarrow B_S^*]$ transitions and cavitation bubbles origination can be stimulated also by IR radiation with frequency, corresponding to the activation energy of corresponding big fluctuations, described in mesoscopic theory by *superdeformons* and *macroconvertons*.

In such a way, using IR radiation and ultrasound it is possible to regulate a lot of different processes in aqueous systems, depending on pH and water activity.

The increasing of ultrasound intensity leads to increased cavitation bubble concentration. The dependence of the resonance cavity radius (R_{res}) on ultrasound frequency (f) can be approximately expressed as:

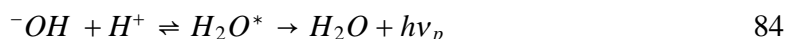
$$R_{\text{res}} = 3000/f \quad 83$$

At certain conditions the water placed in the ultrasound field, begins to shine in the region: 300 – 600nm [15]. This shining is a consequence of electronic excitation of water ions and molecules in the volume of cavitation bubbles.

When the conditions of ultrasound standing wave exist, the number of bubbles and intensity of shining is maximal.

The intensity of shining is nonmonotonically dependent on temperature with maxima around 15, 30, 45 and 65^0 [6]. This temperature corresponds to extremes of stability of primary librational effectons, related to the number of H_2O per effecton's edge (κ) (see comments to Fig. 7a of [1] or to Fig 4a of [2]). An increase of inorganic ion concentration, destabilizing (a)-state of these effectons, elevate the probability of superdeformons and consequently, shining intensity.

The most probable reason of photon radiation is recombination of water molecules, turning it into excited state:



Very different chemical reactions can be stimulated in the volume of cavitation fluctuation by the external fields. The optimal resonant parameters of these fields could be calculated using hierarchic theory.

We propose here that the reaction of water molecules recombination (84) could be responsible for coherent "biophotons" radiation by cell's and microbes cultures and living organisms in visible and ultraviolet (UV) range. The advances in biophoton research are described by Popp et al., 1992 [16].

In accordance to our model, the cell's body filaments - microtubules "catastrophe" (cooperative reversible deassembly) is a result of the internal water cavitation fluctuations due to superdeformons excitation. Such collective process should be accompanied by dissociation and recombination (84) of part of water molecules, localized in the hollow core of microtubules, leading to high-frequency electromagnetic radiation (see Section 17.5 of [1] and paper: Hierarchic model of Consciousness in URL: <http://kftt.karelia.ru/~alexk>). The coherent biophotons in the infrared (IR) range are a consequence of $(a \rightleftharpoons b)_{tr,lb}$ transitions of the water primary effectons in microtubules.

Lot of new theoretical models for different phenomena, based on the same physical model and verified quantitatively by original computer program (copyright

1997, Kaivarainen) confirm our Hierarchic Concept of Condensed Matter.

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