COMPUTERIZED VERIFICATION OF NEW HIERARCHIC THEORY
OF CONDENSED MATTER ON EXAMPLES OF WATER & ICE.

NEW OPTOACOUSTIC DEVICE:
Comprehensive Analyzer of Matter Properties (CAMP)
and its applications

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The short version of new quantum and quantitative Hierarchic theory, general for solids and liquids (Kaivarainen, 1989, 1995, 2001) is presented. Condensed matter is considered as a system of 3D standing waves (collective excitations) of different nature: thermal de Broglie waves (waves B), IR photons, related to intermolecular oscillations and thermal phonons. Theory is verified by computer simulations on examples of pure water and ice, using created computer program (copyright, 1997, Kaivarainen). Good agreement between theoretical and available experimental data of heat capacity, total internal energy, vapor pressure, surface tension, thermal conductivity, viscosity, self-diffusion has been demonstrated for water and ice. Total number of physical parameters of liquids and solids in wide temperature interval, including that of phase transitions, accessible for computer evaluation, is about 300. The evidence of high-T mesoscopic molecular Bose condensation (BC) in water and ice in form of coherent clusters is obtained. Theory unifies dynamics and thermodynamics on microscopic, mesoscopic and macroscopic scales. The idea of new optoacoustic device: Comprehensive Analyzer of Matter Properties (CAMP) with huge informational possibilities, including its various configurations and applications is described. The strong advantage of new device is that only small part of 300 parameters, yielding by CAMP system, is possible to get, using separate experimental methods, like IR spectroscopy, sound velocimetry, densitometry and refractometry. The most of parameters, available using CAMP - computer program, are "hidden", i.e. inaccessible for direct experimental registration. The big amount of basically new information means, that CAMP may provide a real breakthrough in condensed matter and applied physics. Possible applications of CAMP to different technologies and research programs are presented in the last section of this article. This work may be considered as a background of project, involving CAMP-prototype building and testing. The full version of this paper is located at http://arXiv.org/abs/physics/0102086. The series of articles, devoted to different aspects of new theory are placed in the electronic journal "Archive of Los-Alamos": see http://arXiv.org/find/physics/1/au:+Kaivarainen_A/0/1/all/0/1

INTRODUCTION

A quantum based 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 of molecules are related to their translations (tr) and librations (lb).

As the quantum dynamics of condensed matter is anharmonic and does not follow 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 mesoscopic 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 and applying to Virial theorem.

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 mesoscopic Bose condensation (BC), in contrast to macroscopic BC, pertinent for superfluidity and superconductivity.

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 mesoscopic molecular Bose condensates. These consequences of our theory are confirmed by computer calculations.

The 1st order $[gas \rightarrow liquid]$ transition is accompanied by strong decreasing of number of rotational (librational) degrees of freedom due to emergence of primary (lb) effectons and $[liquid \rightarrow solid]$ 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 determined by de Broglie waves length in three selected directions (1, 2, 3), related to symmetry of molecular dynamics. In the case of isotropic molecular motion the effectons' shape is approximated by cube.

The edge-length of primary effectons (tr and lb) is considered as the "parameter of order" in our theory of phase transitions.

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 transitons, 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] *convertons* and *secondary transitons* 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, macrotransitons** 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 simultaneous excitation of **both***: tr* and *lb macrodeformons and macroconvertons* in the same volume means origination 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 (Table). 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.
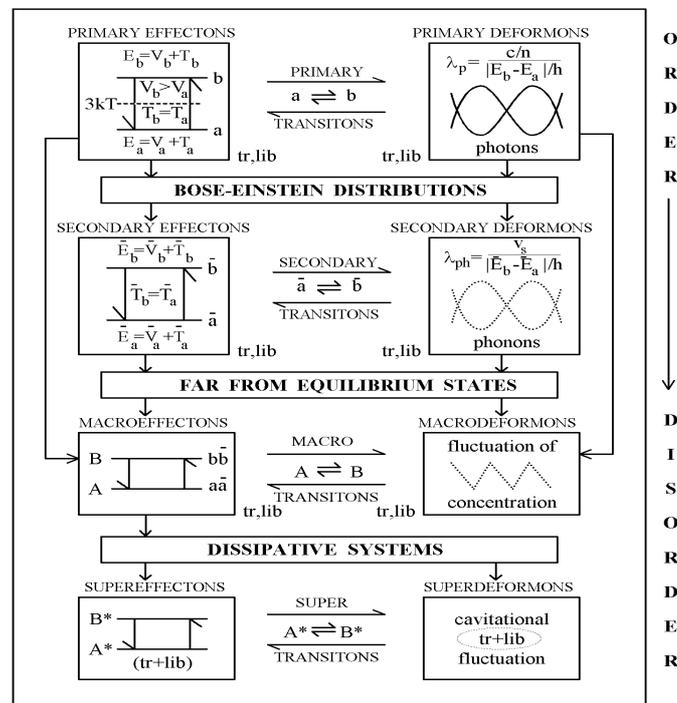

Table. Schematic representation of the 18 types of quasiparticles of condensed matter as a hierarchical dynamic system, based on the effectons, transitons and deformons. Total number of *quasiparticles*, introduced in Hierarchic concept is 24. Six collective excitations, related to *convertons*- interconversions between primary librational and translational effectons and their derivatives are not represented here for the end of simplicity.

The important positive feature of our hierarchic model of matter is that it does not need the

semi-empirical 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 300 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.

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 adjustable parameters.

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

TOTAL INTERNAL ENERGY OF CONDENSED MATTER

The final formula for the total internal energy of (U_{tot}) of one mole of matter, leading from Hierarchic theory, considering condensed matter as a system of 3D standing waves is (see http://arXiv.org/abs/physics/0102086):

$$
\begin{aligned}
U_{\text{tot}} = V_0 \frac{1}{Z} \sum_{tr,lb} &\left\{ \left[\begin{array}{c} n_{ef}\left(P_{ef}^a E_{ef}^a + P_{ef}^b E_{ef}^b + P_t E_t \right) \\ + n_d P_d E_d \end{array} \right] + \right. \\
&+ \left[\bar{n}_{ef}\left(\bar{P}_{ef}^a \bar{E}_{ef}^a + \bar{P}_{ef}^b \bar{E}_{ef}^b + \bar{P}_t \bar{E}_t \right) + \bar{n}_d \bar{P}_d \bar{E}_d \right] + \\
&+ \left[n_M\left(P_M^A E_M^A + P_M^B E_M^B \right) + n_D P_M^D E_M^D \right]_{tr,lb} + \\
&+ V_0 \frac{1}{Z}\left[n_{\text{con}}\left(P_{ac}E_{ac} + P_{bc}E_{bc} + P_{\text{cMt}}E_{\text{cMt}} \right) + \right. \\
&\left. + \left(n_{\text{cda}}P_{ac}E_{ac} + n_{\text{cdb}}P_{bc}E_{bc} + n_{\text{cMd}}P_{\text{cMd}}E_{\text{cMd}} \right) \right] + \\
&\left. + V_0 \frac{1}{Z}n_s\left[\left(P_S^{A^*}E_S^{A^*} + P_S^{B^*}E_S^{B^*} \right) + n_{D^*}P_S^{D^*}E_S^{D^*} \right] \right. \qquad 1
\end{aligned}
$$

The meaning of the variables in formulae (1), necessary for the internal energy calculations, are presented in our paper (Kaivarainen, 2001). Total potential energy of one mole of condensed matter is defined by the difference between corresponding total internal energy and total kinetic energy: $V^{tot} = U^{tot} - T^{tot}$.

It is important to stress, that the same equations are valid for liquids and solids in our theory.

A lot of characteristics of condensed matter, composed from 24 quasiparticles - about 300, may be calculated, using hierarchic theory and CAMP computer program [copyright 1997,

Kaivarainen]. For this end we need four basic input experimental parameters (Kaivarainen, 2001) at the same temperature and pressure:

    1) positions of translational and librational bands in middle/far IR spectrum of condensed matter;

    2) sound velocity;

    3) density or molar volume;

    4) refraction index.

QUANTITATIVE VERIFICATION OF HIERARCHIC THEORY ON EXAMPLES OF ICE AND WATER

Comparison of theoretical temperature dependences of different parameters with experimental data

1. The coincidence of theoretical and experimental data for ice structure stability

Our hierarchic theory makes it possible to calculate unprecedented big amount of parameters for liquids and solids. Part of them, accessible experimentally and taken from literature, are in good correspondence with CAMP - computer simulations.

For example, the calculated minimum of partition function for ice (Z) (Fig. 1a) corresponds to temperature of about -170^0C. For the other hand, the interval from -198 to -173^0C is known, indeed, as T- anomalies one due to the fact that the heat equilibrium of ice establishes very slowly in this range (Maeno, 1988). This fact is a consequence of the less probable ice structure (minimum value of partition function Z) near -170^0C.
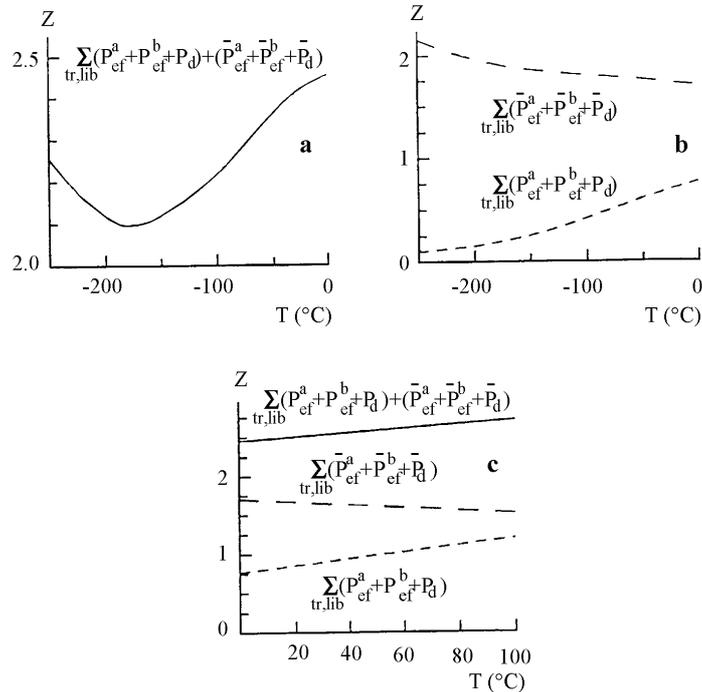

Fig. 1. (a,b,c). Temperature dependences of the total partition function (Z) and contributions related to primary and secondary effectons and deformons for ice (a,b) and water (c).

2. The coincidence of theoretical and experimental heat capacity of ice and water

It follows from Fig. 2a that the mean **theoretical** value of heat capacity for **ice** in the interval from -75 to $0^o C$ is equal to:

$$\bar{C}_p^{ice} = \frac{\Delta U_{tot}}{\Delta T} \approx 39 J/MK = 9.3 \text{ cal}/MK \qquad 2$$

For **water** within the whole range $\Delta T = 100^0 C$, the **theoretical** change in the internal energy is: $\Delta U = 17 - 9.7 = 7.3 kJ/M$ (Fig.2b). This corresponds to mean value of heat capacity of water:

$$C_p^{water} = \frac{\Delta U_{tot}}{\Delta T} = 73 \text{ J/MK} = 17.5 \text{ cal/MK} \qquad 3$$

These results of calculation agree well with the **experimental** mean values $C_p = 18$ Cal/MK for water and $C_p = 9 cal/MK$ for ice (Eisenberg and Kauzmann, 1969).
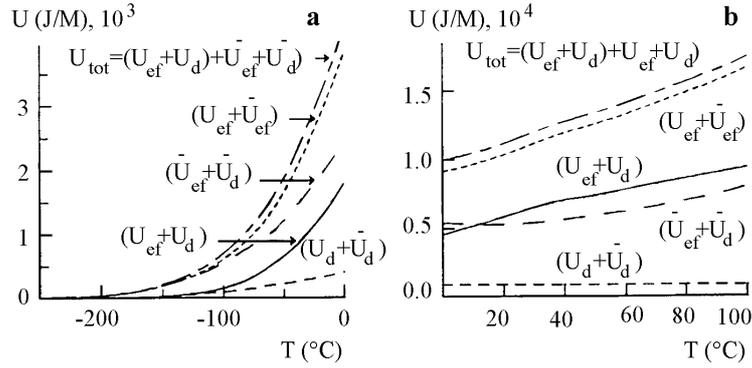

Fig. 2. (a,b). Temperature dependences of the total internal energy (U_{tot}) and different contributions for ice (a) and water (b). Following contributions to U_{tot} are presented: ($U_{ef} + \bar{U}_{ef}$) is the contribution of primary and secondary effectons; ($U_d + \bar{U}_d$) is the contribution of primary and secondary deformons; ($U_{ef} + U_d$) is the contribution of primary effectons and deformons; ($\bar{U}_{ef} + \bar{U}_d$) is the contribution of secondary effectons and deformons.

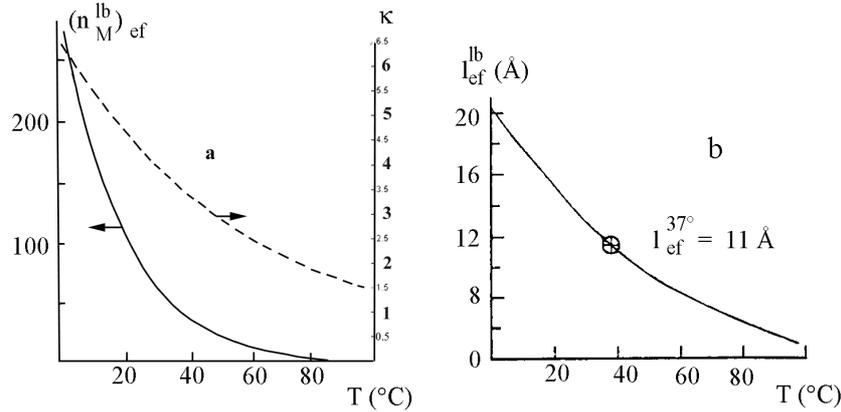### 3. Coincidence between calculated and experimental dimensions of water clusters

Fig. 3. (a) : The temperature dependencies of the number of H_2O molecules in the volume of primary librational effecton (n_M^{lb})$_{ef}$, left axis) and the number of H_2O per length of this effecton edge (κ, right axis); (b): the temperature dependence of the water primary librational effecton (approximated by cube) edge length [$l_{ef}^{lib} = \kappa (V_0/N_0)^{1/3}$].

The number of H_2O molecules within the **primary libration effectons** of water, which could be approximated by a cube, decreases from $n_M = 280$ at 0^0 to $n_M \simeq 3$ at 100^0 (Fig. 3a). It should be noted that at physiological temperatures $(35 - 40^0)$ such quasiparticles contain nearly 40 water molecules. Similar by order dimensions of heavy water clusters (about 10 Å) with

saturated hydrogen bonds were revealed by inelastic neutron scattering method (Texeira et al., 1987).

The dimensions of water clusters are close to dimensions of the open interdomain protein cavities judging from X-ray data. The *flickering* of these clusters, i.e. their (*dissociation* $\rightleftharpoons$ *association*) due to [*lb* $\Leftrightarrow$ *tr*] conversions, in accordance with our model, is directly related to the large-scale dynamics of proteins (Kaivarainen, 1985).

New State Equation for Condensed Matter

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

$$\left(P + \frac{a}{V^2} \right) \left(V - b \right) = RT \qquad\qquad 4$$

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 (4) correctly describes changes in P,V and T related to liquid-gas transitions on the qualitative level. However, the quantitative analysis of (4) 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.

Using our eq. 4.3 (from Kaivarainen, 2001) for the total internal energy of condensed matter (U_{tot}), we can present state equation in a more general form than (4). 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}):

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

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

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

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

where: $U_{ef} = U_{tot}(1 + V/T^t_{kin}) = U^2_{tot}/T_{kin}$ is the effective internal energy and:

$$(1 + V/T_{kin}) = U_{tot}/T_{kin} = S^{-1} \qquad\qquad 7$$

is the reciprocal value of the total structural factor; $P_{tot} = P_{ext} + P_{in}$ is total pressure, P_{ext} and P_{in} are external and internal pressures; $V_{fr} = V_0 - V_{exc} = V_0/n^2$ (see eq.5) is a free molar volume; $U_{tot} = V + T_{kin}$ 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 $P_{in} = 0$; $V_{exc} = 0$; and the potential energy $V = 0$, we get from (6) the Clapeyrone - Mendeleyev equation:

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

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}:

$$P_{in} = \frac{U_{ef}}{V_{fr}} - P_{ext} = \frac{n^2 U^2_{tot}}{V_0 T_{kin}} - P_{ext} \qquad\qquad 8$$

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

and the effective total energy: $U_{ef} = U_{tot}^2/T_{kin} = U_{tot}/S$; where $S = T_{kin}/U_{tot}$ is a total structural factor.

4. Coincidence between calculated and experimental vapor pressure for ice and water

There was not earlier the satisfactory quantitative theory for *vapor pressure* calculation.

We can suggest such a theory using our notion of collective excitations: *superdeformons*, representing the biggest thermal fluctuations (see Kaivarainen, 2001). 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 cavitational 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 semi-empirical surface pressure factor (q^S) as:

$$P_{in}^S = q^S P_{in} = q^S \left(\frac{n^2 U_{tot}}{V_0 S} - P_{ext} \right)$$

9

where: P_{in} corresponds to eq.(8); $S = T_{kin}/U_{tot}$ is a total structure factor.
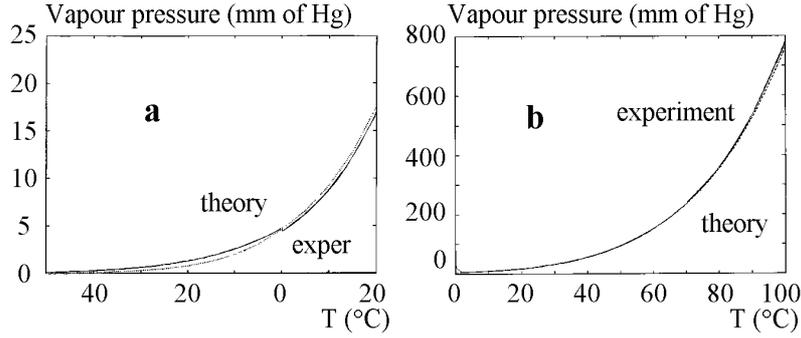

Fig. 4. a) Theoretical (−) and experimental (· ·) temperature dependences of vapor pressure (P_{vap}) for ice (a) and water (b), including phase transition region. The experimental data where taken from Handbook of Chem. & Phys. 67 ed., CRC press, 1986-1987.

Multiplying (9) to probability of superdeformons excitation we obtain for vapor pressure, resulting from evaporation or sublimation, the following formulae:

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

10

where:

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

11

is a probability of superdeformons excitation (see eqs. 3.37, 3.32 and 3.33 from Kaivarainen, 2001).

The pressure surface factor (q^S) could be presented as:

$$q^S = P_{in}^S/P_{in}$$

Theoretical calculated temperature dependences of vapor pressure, described by (10)

coincide very well with experimental ones for water at $q_{liq}^S = 3.1$ and for ice at $q_{sol}^S = 18$ (Fig. 4).

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.

5. Coincidence between calculated and experimental surface tension

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

$$\sigma = (\sigma_{tr} + \sigma_{lb}) \qquad\qquad 12$$

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), taking into account the difference between surface and bulk total energies (q^S), introduced in previous section:

$$\sigma_{tr,} = \frac{1}{\frac{1}{\pi}(Vlb_{ef})_{tr,lb}^{2/3}} \left[\frac{q^S P_{tot}(P_{ef}V_{ef})_{tr,lb} - P_{tot}(P_{ef}V_{ef})_{tr,lb}}{(P_{ef}+P_t)_{tr} + (P_{ef}+P_t)_{lb} + (P_{con}+P_{cMt})} \right] \qquad 13$$

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 vapor pressure calculations; $[P_{tot} = P_{in} + P_{ext}]$ is a total pressure; $(P_{ef})_{tr,lb}$ 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 (13) are the probabilities of corresponding transiton excitation;

$P_{con} = P_{ac} + P_{bc}$ is the sum of probabilities of $[a]$ and $[b]$ *convertons;* $P_{cMt} = P_{ac}P_{bc}$ is a probability of Macroconvertons excitation (see Introduction).

The eq. (13) contains the ratio:

$$(V_{ef}/V_{ef}^{2/3})_{tr,lb} = l_{tr,lb} \qquad\qquad 14$$

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

The resulting surface tension can be presented as:

$$\sigma = \sigma_{tr} + \sigma_{lb} = \pi \frac{P_{tot}(q^S - 1) \cdot \left[(P_{ef})_{tr}l_{tr} + (P_{ef})l_{lb} \right]}{(P_{ef}+P_t)_{tr} + (P_{ef}+P_t)_{lb} + (P_{con}+P_{cMt})} \qquad 15$$

The results of computer calculations of σ (eq. 15) for water and experimental data are presented at Fig.5.
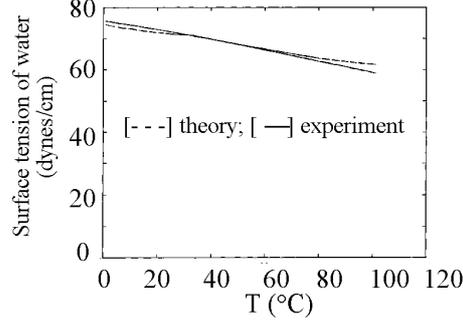
Fig. 5. Experimental (—) and theoretical (---) temperature dependences of the surface tension for water. The experimental data where taken from Handbook of Chem. & Phys., 67 ed., CRC press, 1986-1987.

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.

6. Coincidence between calculated and experimental 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.

Hierarchic 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 $(\kappa_{cd})_{ac,bc}$:

$$\kappa = (\kappa_{sd})_{tr,lb} + (\kappa_{cd})_{ac.bc} = \frac{1}{3} C_v v_s [(\Lambda_{sd})_{tr,lb} + (\Lambda_{cd})_{ac,bc}] \qquad 16$$

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

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

consequently:

$$1/(\Lambda_{sd})_{tr,lb} = \frac{v_s}{(\overline{v}_d)_{tr} + (\overline{v}_d)_{lb}} \qquad 17$$

and free runs of convertons-induced phonons:

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

The heat capacity: $C_V = \partial U_{tot}/\partial T$ can be calculated also from our theory.
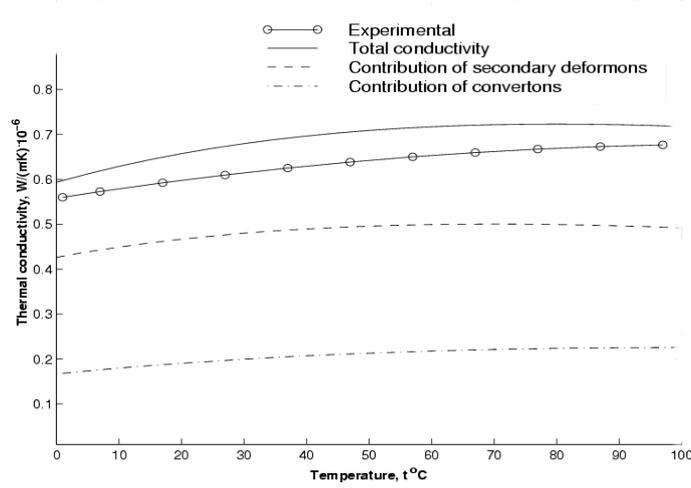
Fig. 6. Temperature dependences of total thermal conductivity for water and contributions, related to acoustic deformons and [*lb/tr*]convertons. The experimental data were taken from Handbook of Chem. & Phys., 67 ed., CRC press, 1986-1987.

7. Coincidence between calculated and experimental 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 new hierarchic/mesoscopic theory of viscosity has been developed.

The dissipation processes, related to $(A \rightleftharpoons B)_{tr,lb}$ cycles of translational and librational macroeffectons and (a,b)-*convertons* excitations were analyzed.

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 (see Kaivarainen, 2001).

The contributions of translational and librational macrodeformons to resulting viscosity are present in following way:

$$\eta_{tr,lb}^{M} = \left[\frac{E_{D}^{M}}{\Delta v_{f}^{0}} \tau^{M} \left(\frac{T_{k}}{U_{tot}} \right)^{3} \right]_{tr,lb} \qquad 18$$

where: (Δv_{f}^{0}) is the reduced fluctuating volume; the energy of macrodeformons: $[E_{D}^{M} = -kT(\ln P_{D}^{M})]_{tr,lb}$.

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

$$\left[\tau^{M} = \tau_{A} + \tau_{B} + \tau_{D} \right]_{tr,lb} \qquad 19$$

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:

$$\left[\tau_{A} = (\tau_{a} \tau_{\overline{a}})^{1/2} \right]_{tr,lb} \quad \text{and} \quad \left[\tau_{A} = (\tau_{a} \tau_{\overline{a}})^{1/2} \right]_{tr,lb} \qquad 20$$

$$\left[\tau_{D} = |(1/\tau_{A}) - (1/\tau_{B})|^{-1} \right]_{tr,lb} \qquad 21$$

Using (18 - 21) it is possible to calculate the contributions of $(A \rightleftharpoons B)$ cycles of translational and librational macroeffectons to viscosity separately.

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

$$\eta^M = \left[\ (\eta)_{tr}^M (\eta)_{lb}^M \ \right]^{1/2} \qquad 22$$

The resulting theoretical viscosity (Fig.8) was calculated as a sum of the averaged contributions of macrodeformons and convertons:
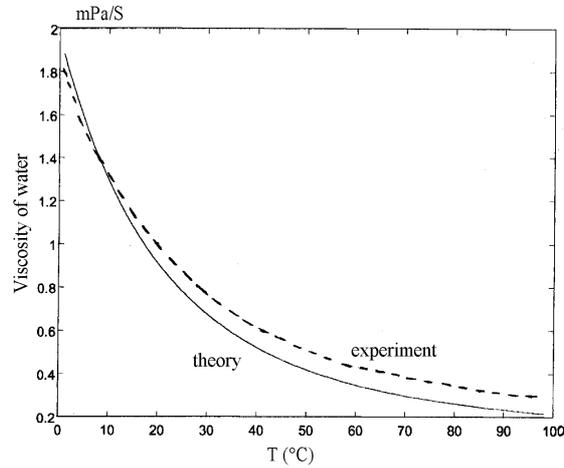
$$\eta = \eta^M + \eta_c \qquad 23$$

Fig. 7. Theoretical and experimental temperature dependences of water viscosity. The experimental data where taken from Handbook of Chem. & Phys. 67 ed., CRC press, 1986-1987.

The theoretical results are in a good accordance with available experimental data.

8. Coincidence between calculated and experimental coefficients of self-diffusion in liquids and solids

Molecular theory of self-diffusion, as well as general concept of *transfer phenomena* in condensed matter also was absent before Hierarchic theory.

The resulting coefficient of self-diffusion in liquids (D) is a sum of the distant (D^M) and local (D_c, D_{Mc}) effects contributions (see eqs.6.64 and 6.67 from Kaivarainen, 2001):
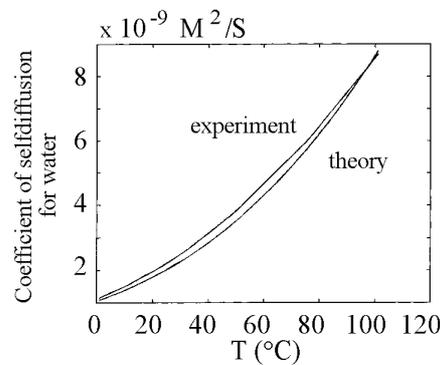
$$D = D^M + D_c + D_{Mc} \qquad 24$$

Fig. 8. Theoretical and experimental temperature dependences of self-diffusion coefficients in water.

The experimental data where taken from Handbook of Chem. & Phys. 77 ed., CRC press, 1996-1997.

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. 8) in temperature interval $(0 - 100^0C)$.

The self-diffusion in solids also may be evaluated using the same approach and CAMP computer program.

The important conclusion, leading from the examples presented above, is that as far the final results of calculations are in a good accordance with experiment, it means that a lot of intermediate parameters, hidden from direct experiment, characterizing the spatial and dynamic properties of number of collective excitations of condensed matter - also correctly describe the matter properties.

The ability of our Hierarchic model to describe quantitatively a lot of parameters of liquids and solids points, that it is valid and general indeed.

9. NEW OPTOACOUSTIC DEVICE, BASED ON HIERARCHIC THEORY:

Comprehensive Analyzer of Matter Properties (CAMP)
[see: www.karelia.ru/~alexk]

The set of formulae obtained in our theory allows to calculate about 300 **physical** parameters of any condensed matter (liquid or solid). Most of them are hidden, i.e. inaccessible for direct experimental measurements.

Simulations evaluation of these parameters can be done using our computer program: CAMP (copyright 1997, Kaivarainen) and the following experimental methods:

1. Far-middle FT-IR or FT-Raman spectroscopy for determination the positions of translational or librational bands: (50-2500) cm-1;

2. Sound velocimetry;

3. Densitometry;

4. Refractometry.

Corresponding data may be obtained at the same temperature and pressure from the SAME SAMPLE (liquid or solid), located in more than one cell and from the same cell for study of nonequilibrium dynamics or kinetic processes.

This leads to idea of new optoacoustic device: Comprehensive Analyzer of Matter Properties (CAMP), which may provide a huge amount of data of any condensed system under study.

The most complicated and expensive component of CAMP is FT-IR or FT-Raman spectrometer or even better their combination for registration of spectra in far and middle region.

The most sensitive parameter is sound velocity.

One of possible CAMP configuration should include special attachment to FT-IR spectrometer (Harrick Scientific Co.), making it possible registration of reflection spectra in far/middle IR region and the refraction index dispersion. Such approach allows to study the properties of samples with strong IR absorption (i.e. aqueous systems) and non transparent mediums. For the other hand, the equipment, provided by Anton-Paar Co., makes it possible a simultaneous measurement of sound velocity and density.

The unified system of modified FT-IR and/or Raman spectrometer, densitometer, sound velocimeter, refractometer, measuring the same sample at similar conditions is necessary to design. Simulation of corresponding parameters, using the interface of such system with personal computer will provide CAMP function.

The another configuration of CAMP may include the FT-Brillouin light scattering spectrometer, based on Fabry-Perrot interferometer. It makes possible simultaneous measurement

of hypersound velocity (from the Doppler shift of side bands of Brillouin spectra) and positions of intermolecular bands [tr and lb] from the Stokes/antiStokes satellite components on the central peak of Brillouin spectra. This means combination of possibilities of Raman spectroscopy and sound velocimetry.

CAMP may allow monitoring of perturbation of very different physical properties of condensed matter under the influence of solute molecules in dilute solutions and external electromagnetic or acoustic fields.

9.1. Possible Applications for Comprehensive Analyzer of Matter Properties (CAMP)

Applications to aqueous systems

1. Monitoring of drinking water and water based beverage (nonalcoholic and alcohol-containing) physical properties, related to taste and biological activity. Modulation of taste by electromagnetic field and vitamins;

2. In pharmaceutical technology - for monitoring of water perturbations, induced by vitamins and drugs at low physiologic concentrations. Correlation of water structure perturbations, induced by vitamins and drugs with biological activity of their aqueous solutions. Such test as the rate of biocells and microbes colony growth may be used for this goal. Regulation of drug-induced effects by electromagnetic and/or acoustic fields;

3. In petrol industry - finding the key physical parameters of benzine, responsible for it octane number.

Searching the ways of cheap treatment of benzine by physical fields or chemicals in low concentrations, increasing the benzine effectiveness;

4. In paper technology - for study of primary colloid systems, containing paper ingredients. Monitoring of influence of electromagnetic and acoustic fields on physical parameters of the bulk and hydrated water, necessary for regulation of [coagulation - peptization] equilibrium of colloids, increasing the quality of paper and coating process;

5. In biotechnology and biochemistry: a wide range of problems, related to role of water in biosystems and water biopolymers interaction (i.e. mechanism of cryoproteins action, detection of specific reactions, like antibody + antigen, enzyme + substrate or inhibitor);

6. In cement technology - for regulation of aqueous colloid systems properties by physical fields, leading to increasing the hardness of cement and bricks;

7. Monitoring of electromagnetic and acoustic pollution, analyzing a physical properties of water in rivers, lakes and sea, as a test system (the ecology problem);

8. Mechanism of transition of flow from the laminar to turbulent one in petroleum pipe-lines and the ways of this process regulation by means of electromagnetic and acoustic fields;

9. Evaluation of frequencies of cavitational fluctuations of water, making it possible their effective resonant stimulation by external physical fields. It may be useful for: a) de-infection of drinking water; b) stimulation of sonoluminescence; c) development of pure energy technology; d) cold fusion stimulation.

Application to nonaqueous systems

1. Fundamental research in all branches of condensed matter physics: thermodynamics, dynamics, phase transitions, transport process, surface tension, self-diffusion, viscosity, vapor pressure, etc.

2. Monitoring of new materials technology (semiconductors, superconductors, polymeric materials) for searching the optimal conditions (T, P, physical fields) for providing the needed parameters on mesoscopic and macroscopic scale;

3. Study of mechanism of high-temperature superconductivity;

4. Study of mechanism of superfluidity.

Comprehensive Analyzer of Matter Properties (CAMP) represents a basically new type of scientific equipment, allowing to get incomparable big amount of information concerning physics of liquids or solids. It can be very useful for investigation of dynamics and mesoscopic

structure of pure matter as well as solid and liquid solutions, the colloid systems and host-guest systems.

The competitive ability of companies, involved in listed above technologies, could be increased strongly, as a result of CAMP application, improving their technology.

The market for Comprehensive Analyzer of Matter Properties (CAMP) is free and due to its unique informational potential could be much bigger than that for IR, Raman or Brillouin spectrometers. It means that the manufacturing of CAMP of different configurations and its marketing also has a big prospects.

The demo-version of CAMP-computer program (CAMP, copyright, 1997*, Kaivarainen) is available and may be ordered from the author or directly downloaded from the front page of web site: www.karelia.ru/~alexk [see also 'Looking for partners'].*

This program demonstrates potential possibilities of basically new optoacoustic device on examples of water and ice.

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