



The influence of radiation emission on the thermodynamic and structural dynamic properties of liquid biosystems

NATALIIA ATAMAS¹, DMYTRO GAVRYUSHENKO¹, VITALY BARDIK¹, KIRILL TARADII¹,
MAXIM LAZARENKO^{1,*}, OLEKSANDER ALEKSEEV¹, JULIE RENEA GEARHEART²,
ANNA MIROSHNICHENKO² and GENNADIY TARANYIK²

¹National Taras Shevchenko University of Kyiv, Kyiv, Ukraine

²Kiev Medical University, Kyiv, Ukraine

*Corresponding author. E-mail: maxs@mail.univ.kiev.ua

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Abstract. The influence of radiation on the thermodynamic properties of liquid systems that are governed by the radiation-induced change in the chemical potentials of the liquid and its components has been studied. The irradiation of coexisting phases in the stationary state is shown to result in a shift of the phase transition point parameters. The temperature shift of the first-order phase transition under the influence of radiation is evaluated with regard to both the entropy and interaction factors in the chemical potential of the system. The results obtained from the MD simulation of the radiation influence on 10% saline quantitatively confirm the predictions of the introduced theoretical model of the irradiation process. To verify our theoretical assumptions concerning modifications in the local structure of the examined saline (water solution of NaCl at 10% concentration), experiments under the influence of irradiation were done.

Keywords. MD simulation; radiation influence; theoretical model; saline; phase transition; multicomponent system.

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1. Introduction

From the beginning, roentgen, X-ray or proton therapies for cancer was pursuing the aim of minimising side effects [1,2]. Processes, which will happen in cells under the influence of radiation, are extremely complicated and lead to various morphological and functional changes of cells, comprising tissues in organs, intracellular and intercellular mediums, blood and lymph [3–5]. These processes are based on the phenomena of ionisation, excitation of atoms and molecules, which appear as a result of the interaction of excitation radiation with the tissues of the organism [6,7]. It is important to underline that in this case the maximum intensity of the interaction of radiation with the tissues of an organism is observed at the primary stage. Consequently, the transmission of excitation is limited to rather short distances, usually,

not always sufficient for the required medical effect in the damaged tissues. It means that in order to achieve the required therapeutic effect, it is necessary to increase the intensity of irradiation or to conduct several courses of therapy, which negatively affects healthy tissues of the organism [8]. For the ray therapy of the deeply located tumours, the medical accelerators of electrons are used. Thus, it is important to stress that one of the main conditions for the successful treatment is the whole period, during which the patient receives a large number of medications, mainly injected intravenously. The medications are diluted in saline, which is the water solution of sodium chloride (NaCl) at a concentration of 10%.

Taking into account the fact that in case of necessity several courses of therapy might take place, it is important to know the consequences of the influence of radiation emission, not only on the damaged tissues, but also

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on the blood plasma and tissue liquids of the organism. Conducting research on the influence of radiation emission, on the physical characteristics of blood plasma and intercellular medium by experimental means appears to be perilous. The main problems are mainly connected with the fact that as a result of the research, the averaged macroscopic characteristics of the system are obtained (density, viscosity, dielectric constant, etc.). These parameters do not provide an answer to the main questions of which energies correspond to the most significant changes of microcharacteristics of blood plasma and tissue liquids, and how to minimise the influence of radiation on these mediums. The usage of molecular modelling along with the non-equilibrium distribution function formalism gives the possibility to overcome these indicated problems. This approach allows the analysis of the processes of interaction in the blood plasma and tissue fluids, based on the analysis of structural changes in the model system of water–NaCl at the concentration of 10% and the energies of irradiation typical for roentgen and ray therapies. The model used in the present work describes only the general properties of particular biological systems. However, the investigation of the influence of radiation emission on this model system allows the formulation of a number of important provisions required for minimising the side effects in roentgen and X-ray therapies for real biological systems.

2. Methods

Speaking of the influence of radiation emission on the macroscopic characteristics of the studied systems, it is important to take into account that the reason for any macroscopic, characteristic change is primarily in the change of microscopic character of the behaviour of the structure elements [9,10]. In the biological systems, along with the change of kinetic coefficients, which are defined by molecular distribution functions of the third order, the influence of radiation emission on phase transitions of various types is a matter of special importance. With sufficient precision, the shift of phase transition parameters, as well the microscopic characteristics of the system, can be evaluated, using only the correlation functions of the second order [11].

3. Result and discussion

3.1 Radiation-induced change of the first-order phase transition temperature

Irradiation of a liquid medium gives rise to an appreciable change in its equilibrium and thermodynamic properties. The thermodynamic properties of the medium are

known to be connected with its structural properties. Owing to irradiation, the thermodynamic equilibrium in the liquid becomes violated, and the liquid structure undergoes a reorganisation. The restoration of the equilibrium structure in a liquid is accompanied by various relaxation processes, mainly the structural relaxation. The equilibrium and non-equilibrium properties of the liquid substantially depend on the character of these relaxation processes [12,13]. However, the issue concerning a detailed analysis of the relaxation processes and the determination of their contribution to the dynamical values of thermodynamic parameters remain open. The state of a liquid system under irradiation is not that of equilibrium, because radiation induces a permanent deviation from the equilibrium. In the framework of the approach proposed in [14], let us consider the case where a biphasic system, which is in the state of thermodynamic equilibrium characterised by the given temperature, pressure and particle number, undergoes irradiation by a source with a constant power. After the time interval of an order of the mean time between the collisions of structural elements (or the characteristic interaction time in liquids), the stochastization of the system takes place, and the distribution function of the particles over their velocities acquires an almost stationary form [15]. Further evolution of the system is exclusively governed by the time dependence of temperature, pressure and radiation source power, irrespective of the initial distribution of molecules in the phase space [16,17]. In this case, according to the Prigogine theorem about the stationary state, the system transits into a state where the entropy production is minimum [18]. In the range of thermodynamic branch stability, using the hypothesis about the existence of local equilibrium [19], one may unambiguously introduce local thermodynamic functions and consider phase transitions in the framework of equilibrium thermodynamics. In the framework of this approach, let us consider the influence of irradiation on the evolution of possible phase transitions of the first kind in liquids. The temperature T_0 and the pressure p_0 of the corresponding phase transition are determined as solutions of equations that describe the required conditions of phase equilibrium. In particular, in the case of a single-component liquid, the equations for boiling and crystallisation look like:

$$\mu_1(T_0, p_0) = \mu_2(T_0, p_0), \quad (1)$$

where $\mu_1(T_0, p_0)$ and $\mu_2(T_0, p_0)$ are the chemical potentials of a single-component medium in the first and second phases at the phase transition point characterised by T_0 and p_0 (the basic systems). Let us consider the case, where the influence of a spatially uniform radiation source with a constant power gives rise to the generation of only one kind of new quasiparticles (excited

molecules) with concentration x_i in the i th phase of the system. It is important to emphasise that in the framework of our approach we do not consider the appearance of charged particles in the system. Then the dependence of the chemical potential $\mu_i(T, p, x_i)$ of the non-excited molecules in this phase on concentration x_i looks like [20]

$$\mu_i(T, p) = \mu_{i0}(T, p) + T \ln[\gamma_i(T, p, x_i)x_i], \quad (2)$$

where $\mu_{i0}(T, p)$ is the chemical potential of the basic system and $\gamma_i(T, p, x_i)$ is the activity coefficient of the subsystem of non-excited molecules. Note that expression (2) is written for the case, where quasiparticles of only one kind are generated under irradiation, but it can be generalised to more complicated cases.

As was mentioned above, the condition of phase equilibrium during the phase transition consists of the equality of the chemical potentials of substances in both phases (1). Under radiation, this relation should be rewritten in the following form:

$$\begin{aligned} \mu_{10}(T_{\text{ref}}, p) + kT \ln[\gamma_1(T_{\text{ref}}, p, x_1)(1 - x_1)] \\ = \mu_{20}(T_{\text{ref}}, p) + kT \ln[\gamma_2(T_{\text{ref}}, p, x_2)(1 - x_2)]. \end{aligned} \quad (3)$$

This equality can be satisfied, only if the phase transition takes place at a new effective temperature T_{ref} (in the general case $T_{\text{ref}} \neq T_0$), provided the pressure is constant. It is easy to see that, if excited molecules are available, the curve describing the temperature dependence of the chemical potential (the Gibbs thermodynamic potential) of the liquid shifts by a value that describes the corresponding change of the chemical potential. As the concentrations of the excited molecules are very low, it is evident that the deviation δT of the effective phase transition temperature T_{ref} from the basic T_0 is also small ($(|\delta T|/T_0) \ll 1$). Therefore, expanding μ_{i0} and γ_i in expression (3) in power series of $\delta T/T_0$ up to linear terms, we obtain the following expression for the relative variation of the phase transition temperature:

$$\begin{aligned} \frac{\delta T}{T_0} = kT_0 \left[\ln \frac{1 - x_1}{1 - x_2} + \ln \frac{\gamma_1}{\gamma_2} \right] \\ \times \left[q - kT_0 \left\{ \ln \frac{1 - x_1}{1 - x_2} \right. \right. \\ \left. \left. + \ln \frac{\gamma_1}{\gamma_2} \right\} - kT_0^2 \left\{ \left(\frac{\partial}{\partial T} \ln \gamma_1 \right)_{p, x_1} \right. \right. \\ \left. \left. - \left(\frac{\partial}{\partial T} \ln \gamma_2 \right)_{p, x_2} \right\} \right]^{-1}. \end{aligned} \quad (4)$$

To calculate $\delta T/T_0$, we have to know the dependence of the activity coefficients γ_i on pressure and concentration, which are associated with the features in the

equation of system state. In this work, we confine the consideration to the cases of an ideal solution, which means accounting for only entropic factors and a regular solution, whose model involves both entropic and energy contributions.

3.2 Ideal solution

Let us consider the case where the solution is ideal. In many systems, the solution of the excited and unexcited particles with an arbitrary concentration of the former can be considered ideal to a high accuracy, because the components (excited and unexcited molecules) are rather similar to one another with respect to the interaction between the molecules, as well as to their shapes and dimensions [21]. In addition, the solution can often be regarded ideal when $x_i \ll 1$. In the framework of this model, the contribution of entropic factors to the thermodynamic potentials at the mixing of unexcited and excited molecules dominates over the energy factors, so that the latter can be neglected. In this case the activity coefficient is identically equal to unity, and the following expression is obtained for the relative temperature shift $(\delta T/T_0)_{id}$:

$$\left(\frac{\delta T}{T_0} \right)_{id} = \frac{kT_0 \ln \frac{1-x_1}{1-x_2}}{q - kT_0 \ln \frac{1-x_1}{1-x_2}}. \quad (5)$$

The analysis of this expression demonstrates that, if the concentration of the excited particles is low, the dependence of the temperature shift on x_1 or x_2 is linear. At the same time, the sign of δT can change, if x_2 is fixed, but the particle concentration in the other phase, x_1 , is varied.

Formula (5) makes it possible to evaluate $(\delta T/T_0)_{id}$. For instance, for liquid argon coexisting with its saturated vapour at the temperature $T_0 = 87.2$ K and the pressure $p_0 = 1.01 \cdot 10^5$ Pa, δT can reach a value of 0.12 K at $x_2 \approx 0.01$. Such concentrations of excited particles are feasible for micro and nanosystems [22].

Let us consider the case of the ‘liquid–vapour’ phase equilibrium. Subscript 2 will be used to denote the liquid phase and subscript 1 denotes the vapour phase. The concentration of the excited molecules depends on the rate of their generation and the rate of their decay, i.e. on their lifetime. The generation rate for the excited molecules is proportional to the density of the medium and the excitation cross-section. In the case of the ‘liquid–vapour’ phase equilibrium, the density of the liquid is larger than that of the vapour [23]. However, the lifetime of the vapour molecules in the excited state can be much longer than that of the excited state of the molecules in the liquid, for example, if it is determined by the collisions of molecules. Therefore, for a single-component medium

where the lifetime of the excited state of the vapour molecules does not exceed the lifetime of the excited state of molecules in the liquid, the relation $x_2 > x_1$ is satisfied, i.e. the boiling temperature increases. Otherwise, the relation $x_2 < x_1$ can be applied. In this case, the boiling temperature decreases.

Now let us consider the case of the ‘liquid–solid’ phase equilibrium. Subscript 2 denotes the solid state and subscript 1 denotes the liquid state. The densities of the liquid and solid phases of the medium, as well as the excitation cross-sections of molecules in the liquid and solid phases, are almost identical. However, the lifetime of the excited state of molecules in the solid phase, as a rule, is much shorter than that in the liquid, which is related to the fact that, due to the existence of the crystal lattice in a solid, the excitation energy of a molecule can be rapidly redistributed between other molecules of the crystal. As a rule, $x_2 < x_1$, so that the melting temperature decreases. However, for some reasons, if the opposite case takes place, the melting temperature increases. Again, the case $T = T_0$ may exist, which is realised, provided $x_2 = x_1$.

Finally, let us consider the case of the ‘gas–solid’ phase equilibrium. Now, subscript 2 will be used to denote the solid phase and the subscript 1 the gas phase. The excitation cross-sections of molecules in the gas and solid phases of a single-component medium are almost identical. The density of the solid phase considerably exceeds that of the gas phase, but the lifetime of the excited state of molecules in the solid phase is usually considerably shorter than that in the gas phase. Therefore, for a single-component medium, various ratios between the numbers of excited molecules in those phases are possible, depending on the specific values of the generation and decay rates for the excited molecules in the gas and solid phases. If $x_2 > x_1$, the sublimation temperature increases; otherwise, it decreases.

3.3 Regular solution

Let us consider the case of a regular solution. The model of a regular solution adequately describes the thermodynamic behaviour of electrolyte solutions, but it is also applicable to solid solutions of metals. The activity coefficient of a regular solution can be written in the following form:

$$kT \ln \gamma_i(T, p, x_i) = \frac{a^{(i)}(p)}{2} x_i^2. \quad (6)$$

Here, with the help of the thermodynamic perturbation theory, the coefficient $a^{(i)}(p)$ can be presented as a combination of integrals $\Phi_{\alpha\beta}^i(T, p)$ from the radial

distribution function of the basic system, $g_{20}^i(\vec{R}, T, p)$ [24]:

$$\frac{a^{(i)}(p)}{kT} = 2\Phi_{\alpha\beta}^i - \Phi_{\alpha\alpha}^i - \Phi_{\beta\beta}^i, \quad (7)$$

$$\Phi_{\alpha\beta}^i = \rho_0(p, T) \int_{\langle V(p, T, N) \rangle_0} d\vec{r} g_{20}^i(\vec{R}, T, p) \times \left[\exp\left(-\frac{\varphi_{\alpha\beta} - \varphi_0}{kT}\right) - 1 \right], \quad (8)$$

where $\rho_0(p, T)$ is the numerical density of the basic system, $\varphi_{\alpha\beta}$ is the interaction potential between the particles of the α th and β th kinds and φ_0 is the interaction potential between particles of the basic system.

In the case of a regular solution, on the basis of formula (4), the following expression can be obtained for a relative shift of the phase transition temperature:

$$\left(\frac{\delta T}{T_0}\right)_{\text{reg}} = \left(\frac{\delta T}{T_0}\right)_{\text{id}} + \frac{\frac{a^{(1)}x_1^2}{2} - \frac{a^{(2)}x_2^2}{2}}{q - kT_0 \ln \frac{1-x_1}{1-x_2}}. \quad (9)$$

Hence, this quantity is divided into two terms. The first term is associated only with entropic effects, i.e. with the appearance of new particles in the solution that differ from the basic particles in any, even non-force, characteristics. The second term is connected with a modification of the interaction potential between the excited particles. At low concentrations of excited particles, the first term in this parameter is linear, whereas the second is quadratic, which gives rise to the smaller influence of the latter on a shift of the phase transition temperature.

In order to evaluate the contribution of energy factors to a shift of the phase transition temperature according to expressions (7)–(9), we have to know, in addition to the thermal equation of state for the basic system, its radial distribution function, $g_{20}^i(\vec{R}, T, p)$, as well as the potentials of pair interactions ‘excited particle–excited particle’ and ‘excited particle–unexcited particle’. The radial distribution function of argon atoms was found, by using numerical simulation in the framework of a canonical ensemble and applying the molecular dynamics methods. The molecular dynamics method was realised with the help of the modified software package DL POLY 4.05 [25]. The time step was selected to be equal to 1 fs. The cubic cell contained 216 interacting particles. Periodic boundary conditions were imposed. The volume of a unit cell in the examined system was calculated in accordance with the experimental values obtained for the solution density at the required temperature. The molecule-to-molecule interaction was described, using the Lennard–Jones interatomic potential [26,27].

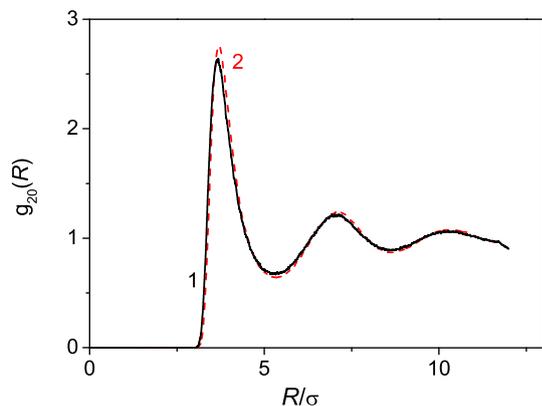


Figure 1. Radial distribution functions for argon atoms at pressure $p_0 = 1.01 \cdot 10^5$ Pa and temperatures of 83 K (solid curve 1) and 87 K (dashed curve 2).

The radial distribution functions of argon atoms at two temperatures are depicted in figure 1. The results were obtained using the molecular dynamics methods. They allow us to determine that, in the case of argon at temperature $T_0 = 87.2$ K and pressure $p_0 = 1.01 \cdot 10^5$ Pa, the temperature shift of the ‘liquid–vapour’ phase transition amounts to $(\delta T)_{\text{reg}} \approx 0.11$ K at $x_1 \approx 10^{-7}$ (gas) and $x_2 \approx 0.01$ (liquid). The results obtained for the temperature shift of the first-order phase transition under irradiation testify that in the framework of the proposed approach, the entropic contributions to this quantity play a dominant role. At the same time, the energy contributions (the regular solution) give rise to only an insignificant temperature shift of the phase transition in the system.

3.4 Computer experiment

Experiments were done to verify our theoretical assumptions concerning modifications in the local structure of the examined saline (NaCl aqueous solution at 10%) under the influence of the irradiation. The results were compared with the predictions of the theoretical model suggested earlier. Intermolecular interaction in the saline liquid model systems was described, using the following potential [26]:

$$\begin{aligned}
 U_{\text{sum}} &= U_{\text{LJ}} + U_{\text{Coul}} \\
 &= \sum_{ij} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}} \right)^6 \right] \\
 &\quad + \sum_{ij} \frac{q_i q_j}{R_{ij}}, \quad (10)
 \end{aligned}$$

where σ_{ij} , ε_{ij} are the parameters of Lennar–Jones interaction, R_{ij} is the distance between interaction particles

and q_i is the charge of the i th particle. MD simulations were performed using DL_POLY software [27] with the time step of 2 fs. Stabilisation was conducted in NVT ensemble, a cubical cell with 256 interacting particles and 1 He particle at $T = 300$ K with periodical boundary conditions. The volume of the elementary cell of the studied system was calculated according to the experimentally defined values of density of the saline at $T = 300$ K. The electrostatic interaction at long distance was represented by Ewald summarisation [28]. Influence of radiation emission on the studied system was analysed according to the method proposed in [29] by the following scheme: stabilisation of the system in NVT ensemble was attained making $8 \cdot 10^5$ steps of calculation. Irradiation was included by accelerating the He atom present in the system. Next, the radiation was switched on. Afterward, one He particle was subjected to the irradiation with energy in the interval of (0–12) MeV. At this stage, a simulation was performed in the NVE ensemble. The energy of the He particle was equally distributed along all the coordinate axes. In order to reach stationary state of the system, the energy was added discretely with the step 1.0 MeV. It was done by accelerating He every 2 ps to have the total irradiation energy range of (0–12) MeV. The system was again allowed to come to the equilibrium state for 10^6 calculation steps. Then, several series of independent calculations with time steps of 200, 160 and 80 fs were carried out to obtain the energy characteristics of the studied system. All radial distribution functions (RDFs), which characterise the probability distribution density for various classes of interactions between particles and make it possible to discern interactions that are the most sensitive to the influence of radiation, were determined with a step of 200 fs.

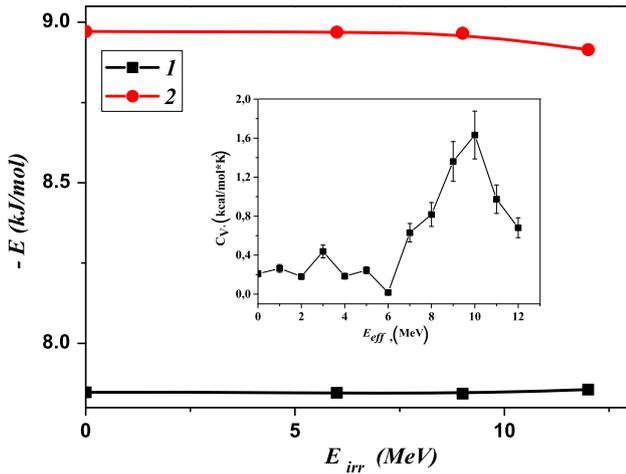
All the parameters for the atoms of molecules of water, ions and He of the simulation process are given in table 1.

Cations, anions and molecules of water were represented as hard, charged modelling systems. The interaction between molecules of water and ions was described using the OPLS-potentials. The interaction of water–water molecules was described using the SPC/E model [29]. The interaction parameters between particles of various kinds were determined using the combinatory rule [26].

The obtained dependencies of the total energy of interatomic interactions $\langle E_{\text{sum}} \rangle$ and its components ($\langle E_{\text{Coul}} \rangle$, which characterise the Coulomb interaction and $\langle E_{\text{LJ}} \rangle$, which characterises van der Waals interaction) from the energy of irradiation E_{irr} obtained for the solution are presented in figure 2. The obtained dependencies give evidence that further increase in the irradiation energy up to 6 MeV does not lead to the increase of the values of $\langle E_{\text{sum}} \rangle$ in the studied system. The increase of E_{irr} up to

Table 1. Charges q_i , Lennard–Jones parameters σ_{ij} , ε_{ij} , masses M [25,26].

Atom	q (e)	σ_{ij} (Å)	ε_{ij} (kcal·mol ⁻¹)	M (a.u.m.)
H	0.4238	0.0	0.0	1
O	-0.8436	3.169	0.6502	15.990
Na ⁺	+1	2.35	0.1	39.098
Cl ⁻	-1	4.4	0.1	35.453
He	+2	2.6	0.084	4.0026

**Figure 2.** Dependence of $\langle E_{\text{sum}} \rangle$ (1) and its Coulomb part $\langle E_{\text{coul}} \rangle$ (2) from E_{irr} for saline at $T = 300$ K. Inset: Dependence of heat capacity of saline from E_{irr} at $T = 300$ K.

10 MeV leads to the increase of $\langle E_{\text{coul}} \rangle$; further increase of E_{irr} to 12 MeV leads to the decrease of the values of $\langle E_{\text{coul}} \rangle$. The obtained data allow the supposition that $E_{\text{irr}} < 6$ MeV does not influence the structure of a liquid. By turn, further increase of E_{irr} from 12 MeV and higher leads to the change of $\langle E_{\text{sum}} \rangle$. It is important to note that the change of $\langle E_{\text{sum}} \rangle$ correlates with the change of $\langle E_{\text{coul}} \rangle$. The slight gradual increase in $\langle E_{\text{coul}} \rangle$ values in the range of $E_{\text{irr}} = (6-12)$ MeV gives evidence of the increase of the long-range Coulomb interactions in the studied system. The dependency of the energy characteristics in the studied systems from E_{irr} allows the supposition that $E_{\text{irr}} > 6$ MeV can influence the structure and dynamics of the systems formed by ions and molecules of water, and also cause the reformation of the network of hydrogen bonds in the studied system. In order to check this assumption, the dependency of heat capacity C_V of saline from E_{irr} (inset of figure 2) was obtained. In order to calculate the value of heat capacity, the value of $\langle E_{\text{sum}} \rangle$ was used according to the

equation [26]

$$C_V = \frac{\langle \Delta E_{\text{sum}}^2 \rangle_{NVT}}{kT^2}, \quad (11)$$

where k is the Boltzmann constant. The obtained dependence C_V is maximum when $E_{\text{irr}} = 9$ MeV. The reason of the appeared maximum may be due to the alteration of the local structure of the studied system, namely, the alteration of the form of water clusters, number of molecules, which form these clusters, as well as the decrease of the influence of the ionisation processes.

The analysis of the RDF with simulation obtained from MD can allow exact estimation of the influence of the value of E_{irr} on the alteration of the local structure of saline. Primarily, let us consider and analyse RDFs, which describe the probability of the location of the water molecules relative to one another. RDF $G^{\text{OW-OW}}(R)$ (figure 3a), the location of the first maximum, is associated with the distance between the molecules of water. It shows that under the influence of E_{irr} the distance between the interacting water does not change. Similarly, the length of hydrogen bonds (HB) between water molecules remains unaltered, which is supported by the fact that the first and the second maximums of RDF $G^{\text{OW-HW}}(R)$ (figure 3b) also do not change. Still, the invariability of the location of the first and the second minimums of RDF $G^{\text{OW-HW}}(R)$ and $G^{\text{OW-OW}}(R)$ give evidence of the independence of the size of the first and the second hydration spheres from E_{irr} . The received data indicate that the irradiation leads to the change in the number of molecules, which form water clusters. It should be noted that under irradiation the ionisation processes take place, leading to the destruction of HB in the water molecule itself and to the formation of free hydrogen (H^+) atoms and hydroxyl groups (OH^-). Taking account of these facts, it is possible to conclude that the network of HB loses its percolation properties under the influence of radiation. That is, in the saline, independently of the values of energy of irradiation, the following components can be present: clusters formed by the molecules of water, the

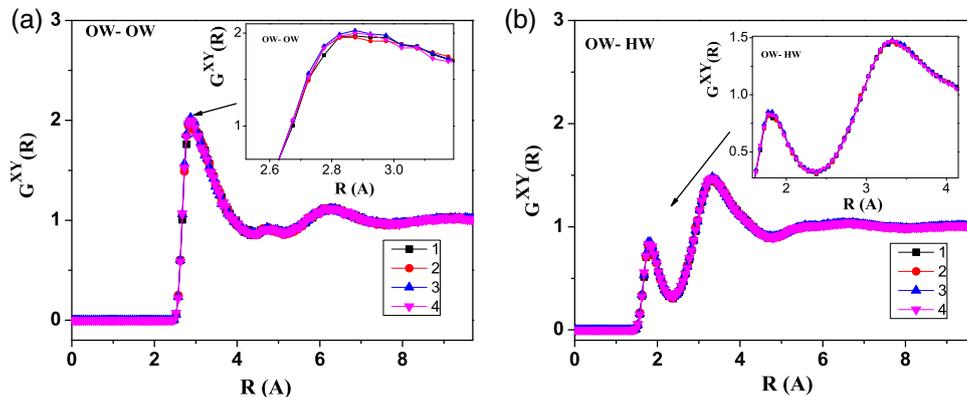


Figure 3. $G^{OW-OW}(R)$ (a) and $G^{OW-HW}(R)$ (b) RDFs for $E_{irr} = (0-12)$ MeV (1 – 0 MeV, 2 – 6 MeV, 3 – 9 MeV, 4 – 12 MeV) in saline at $T = 300$ K.

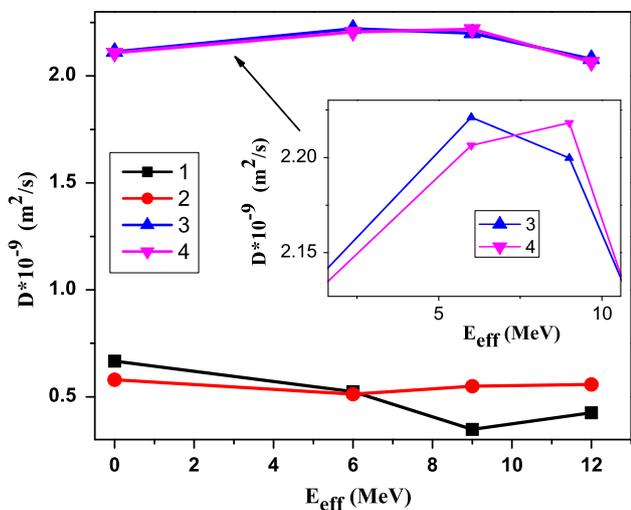


Figure 4. Dependence of self-diffusion coefficient D (1 – D^{Na^+} , 2 – D^{Cl^-} , 3 – D^H , 4 – D^{OH}) from E_{irr} in saline at $T = 300$ K.

structure of which does not depend on the energy of irradiation, free hydrogen atoms (H^+) and hydroxyl groups (OH^-). To find the physical mechanism of the radiation influence on the water in saline causing the observed dynamic changes, the obtained simulation results are compared with the changes of the self-diffusion coefficients of water and ions, which are calculated by integrating the VAF [26].

From the analysis of the data presented in figure 4, it follows that in the energy range $E_{irr} < 2$ MeV the percentage of ionised molecules is rather small, which points out that the self-diffusion coefficient D^H for the hydrogen atom of a molecule of water H^+ and D^{OH} for the group OH^- of water are approximately the same. That is, at these energies of irradiation the molecules of water were not affected by ionisation. When $E_{irr} > 2$ MeV the values of the diffusion coefficient D^H and D^{OH} are different, which supports the assumption that

ionisation takes place, breaking the water molecules under the influence of irradiation, thus leading to the restructuring of the network of HB between molecules of water.

The further increase of E_{irr} to 6 MeV leads to the increase of the values of the self-diffusion coefficient of water (D^{H_2O}), which gives evidence of the increase of the mobility of subsystems, consisting of water molecules, the increase of the free hydrogen atoms (H^+) of molecules of water and of hydroxyl groups (OH^-) of water molecules, and as a result, the reorganisation of the local structure of liquid. The further increase of E_{irr} to 9 MeV does not change the values of D^{H_2O} . Consequently, it is possible to assume that in the range of $E_{irr} = (6-9)$ MeV, the stabilisation of the local structure of the studied systems is observed. The further increase of E_{irr} to 9 MeV is followed by the decrease of the values of D^{H_2O} . That is, at these energies the movement of water molecules is impeded, and the values of D^{H_2O} at $E_{irr} = 9$ MeV and D^{H_2O} at $E_{irr} = 0$ MeV are the same. This concurrence may be due to the formation of water molecules and the stabilisation of the network of HB between these molecules.

The analysis shows that the main contribution in the alteration of structural dynamic properties of saline under the influence of irradiation can be caused both by the changes of the structural properties of water and subsystems formed by ions and by the changes of structural properties of subsystems formed by ions and water molecules. Of $G^{Cl^-OW}(R)$ and $G^{Cl^-HW}(R)$ (figures 5a and 5b) the second one is of special interest. The first maximum of $G(R)^{Cl^-HW}$ is located at a distance of 2.2 Å and HB complexes with the hydrogen atom of a molecule of water can form between interacting particles. The length of these complexes does not depend on E_{irr} . The values of RDF increase with the increase of E_{irr} up to 9 MeV. The analysis of RDFs $G^{Na-OW}(R)$ (figure 6a) and $G^{Na-HW}(R)$ (figure

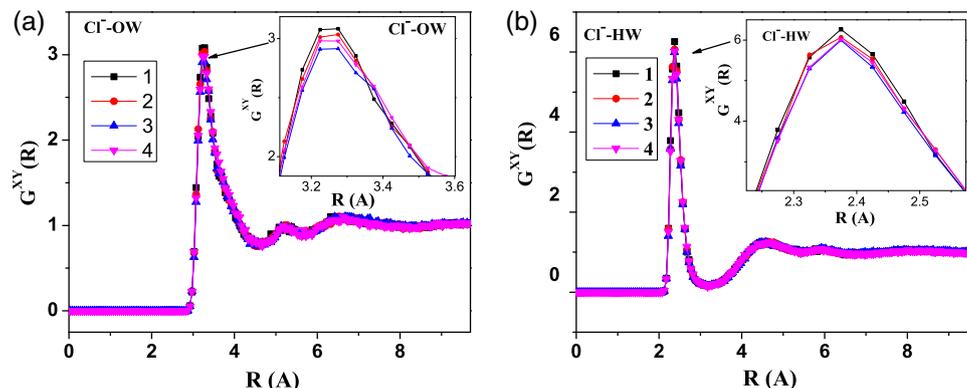


Figure 5. $G^{\text{Cl-OW}}(R)$ (a) and $G^{\text{Cl-HW}}(R)$ (b) RDFs for $E_{\text{irr}} = (0-12)$ MeV (1 – 0 MeV, 2 – 6 MeV, 3 – 9 MeV, 4 – 12 MeV) in saline at $T = 300$ K.

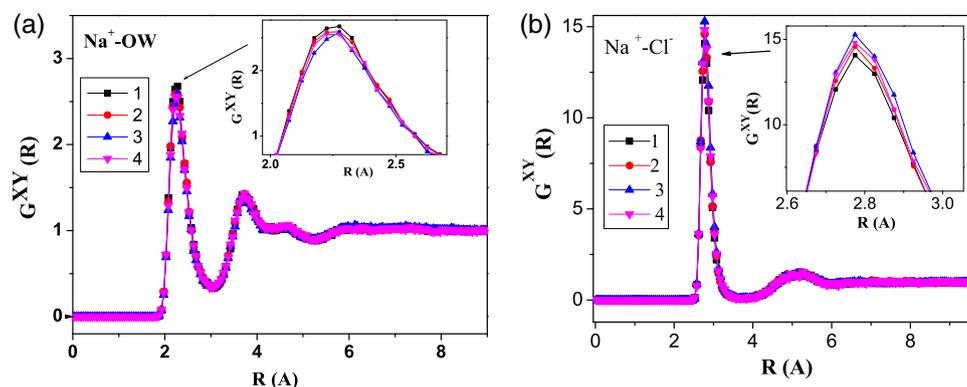


Figure 6. $G^{\text{Na-OW}}(R)$ (a) and $G^{\text{Na-Cl}}(R)$ (b) RDFs for $E_{\text{irr}} = (0-12)$ MeV (1 – 0 MeV, 2 – 6 MeV, 3 – 9 MeV, 4 – 12 MeV) in saline at $T = 300$ K.

S1(electronic supplementary information (ESI))) allows definition of the role of irradiation on the interaction of cations with molecules of water $\text{Na}\dots\text{O}^{\text{W}}$, $\text{Na}\dots\text{H}^{\text{W}}$, where the first maximums of RDFs $G^{\text{Na-OW}}(R)$ and $G^{\text{Na-HW}}(R)$ are fixed at the distances of 2.3 \AA and 3.1 \AA correspondingly. In both cases, the locations and values of the first and the second minimums of RDF remain unaltered, giving evidence of the independence of the sizes of the first and the second hydration spheres from E_{irr} . The location of the first maximum of RDF $G^{\text{Na-Cl}}(R)$ (figure 6b) does not depend on E_{irr} , and consequently, the distance between the interacting particles independently of the values of E_{irr} . At $E_{\text{irr}} \sim 9$ MeV the anomalous behaviour of RDFs is detected; the anomalous increase of RDF $G^{\text{Cl-Cl}}(R)$ (figure S2(ESI)) values and the decrease of the values of the first minimum are detected. This decrease shows that the local structure of the studied system is highly ordered at $E_{\text{irr}} \sim 9$ MeV. When Na^+ cations interact with each other, the increase of RDF $G^{\text{Na-Na}}(R)$ (figure S3(ESI)) values is also detected at $E_{\text{irr}} = 9$ MeV, and the size of the first hydration sphere can be defined more precisely. Such behaviour qualitatively confirms our hypothesis that one

of the important mechanisms of the influence of irradiation on the properties of saline is the change of the structure of liquids.

From the analysis of the self-diffusion coefficient (figure 4), D^{Cl} remains almost constant and D^{Na} decreases as E_{irr} increases from 0 up to 6 MeV. When $E_{\text{irr}} < 9$ MeV, the reconfiguration of the local structure of the solution in the vicinities of anions runs more slowly than in the vicinities of cations, which is related to substantial differences between the masses and the Stokes radii of those anions and cations (in particular, the Stokes radius equals 1.9 \AA for Na^+ and 1.3 \AA for a Cl^-). As E_{irr} increases from 6 to 9 MeV, an insignificant reduction of $D^{\text{H}_2\text{O}}$ takes place. The mobility of ions increases at that, whereas the mobility of cations substantially decreases. The reduction of D^{Na} values testifies that almost all cations participate in the formation of associates with other solution components at this E_{irr} . A further increase of E_{irr} to 12 MeV stimulates the growth of D^{Na} , which remains, nevertheless, much lower than D^{Cl} . In other words, at $E_{\text{irr}} < 9$ MeV, the mobility of water molecules in the system does not change. Further increase of E_{irr} gives rise to a reduction of $D^{\text{H}_2\text{O}}$ values, indicating that

the free motion of water molecules becomes more complicated.

4. Conclusions

The action of radiation on a liquid system gives rise to an increase of the configurational entropy of the system. As a result, the chemical potentials of the components of a system change, which in turn gives rise to the temperature shift of the first-order phase transitions. Depending on the properties of the medium in various phases (density, scattering and excitation cross-sections, lifetime of the excited molecules, and so on) and on the radiation parameters, the phase transition temperature may shift at a constant pressure. The entropic contributions to changes of the thermodynamic potentials under irradiation play a dominant role in shifting the phase transition temperature in the system. At the same time, accounting for the energy contributions (the non-ideality of a solution) leads to only an insignificant shift of this temperature. It is accepted that irradiation of the fluid system, an external source, leads to changes of the local structure of liquid saline systems. MD calculations showed that at E_{irr} , other than 9 MeV, there are no cardinal structural changes of the studied system, whereas at $E_{\text{irr}} = 9$ MeV there are cardinal changes of local structure and dynamics of the studied solution.

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References

- [1] A Brahme, *Introduction to the development of radiation therapy optimization, in biologically optimized radiation therapy* (Karolinska Institutet, Sweden, 2014)
- [2] A Pompos, M Durante and H Choy, *JAMA Oncol.* **2**(12), 1539 (2016)
- [3] A Chaikh, J Ojala and C Khamphan, *Radiat. Oncol.* **13**, 60 (2018)
- [4] R Mohan and D Grosshans, *Adv. Drug. Deliv. Rev.* **109**, 26 (2017)
- [5] X Jia, T Pawlicki and K Murphy, *Transl. Cancer Res.* **1**, 207 (2012)
- [6] J P Gerard, R J Myerson and A S Myint, *Expert Rev. Med. Devices* **8**(4), 483 (2011)
- [7] J Thariat and J L Habrand, *Bull. Cancer.* **105**(3), 315 (2018)
- [8] E J Henley and E R Johnson, *The chemistry and physics of high energy reaction* (Washington D.C., Washington, 1969)
- [9] L Bulavin, D Gavryushenko and V Sysoev, *Ukr. J. Phys.* **52**(10), 934 (2007)
- [10] H M Momen, *Pramana – J. Phys.* **87**(2): 26 (2016)
- [11] Yu Kalyuzhnyi, S Cui and T Cummings, *Phys. Rev. E* **60**(12), 1716 (1999)
- [12] O M Alekseev, Y F Zabashta, V I Kovalchuk, M M Lazarenko and L A Bulavin, *Ukr. J. Phys.* **60**(3), 238 (2019)
- [13] O M Alekseev, Y F Zabashta, V I Kovalchuk, M M Lazarenko, E G Rudnikov and L A Bulavin, *Ukr. J. Phys.* **65**, 50 (2020)
- [14] D A Gavryushenko and K V Taradii, *Ukr. J. Phys.* **60**, 763 (2015)
- [15] D N Zubarev, *Nonequilibrium statistical thermodynamics* (Consultants Bureau, New York, USA, 1974)
- [16] P Glansdorff and I Prigogine, *Am. J. Phys.* **41**(3), 147 (1973)
- [17] M Kac, Probability and related topics in physical sciences, in: *Lectures in applied mathematics* (Interscience, New York, USA, 1959) Vol. 1
- [18] S Ruurds de Groot and P Mazur, *Non-equilibrium thermodynamics* (Courier Corporation, Amsterdam, North-Holland, 1963)
- [19] D Kondepudi and I Prigogine, *Modern thermodynamics: From heat engines to dissipative structures*, 2nd edn (John Wiley and Sons, New Jersey, USA, 2014)
- [20] K Trachenko, J M Runeda, E Artacho and T Dove, *Phys. Rev. B* **71**, 184104 (2005)
- [21] M Chiapetto, C S Becquart, C Domain and L Malerba, *Proceedings of the 12th International Conference on Computer Simulation of Radiation Effects in Solids* (Elsevier, Amsterdam, Netherlands, 2015) Vol. 352, p. 56
- [22] V M Sysoev and S A Terletskii, *Zh. Fiz. Khim.* **58**, 370 (1984)
- [23] S Ushcats, M Ushcats, L Bulavin, O Svechnikova and I Mykheliev, *Pramana – J. Phys.* **91**: 31 (2018)
- [24] I Todorov, W Smith and K Trachenko, *J. Phys.: Condens. Matter* **16**, S2623 (2004)
- [25] M P Allen and D Y Tildesley, *Computer simulation of liquids* (Clarendon Press, Oxford, UK, 2010)
- [26] E Zarkadoula, R Devanathan, W J Weber, M A Seaton and I T Todorov, *J. Appl. Phys.* **115**, 083507 (2014)
- [27] T Schlick, Molecular modeling and simulation: An interdisciplinary guide, in: *Interdisciplinary Applied Mathematics, Mathematical Biology* (Springer-Verlag: Berlin, Heidelberg, New York, USA, 2002)
- [28] K Trachenko, M Dove and E Salje, *Mol. Sim.* **31**, 355 (2005)
- [29] P Balbuena, K Johnston and P Rossky, *Phys. Chem.* **100**, 2706 (1996)