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## RADIATION EFFECT ON THE CHEMICAL POTENTIAL OF MODEL LIQUIDS

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*Irradiation, in particular with electromagnetic radiation, is one of the factors affecting the molecular mechanisms of physiological processes in the human body. In most cases, this influence manifests itself via a change in the chemical composition (radiolysis) or local heating, which invokes nonequilibrium processes. Modern approaches to studying these effects are based on modeling changes in the configurational entropy and chemical potentials of liquids under irradiation. Within this framework, a liquid is considered a two-component solution of excited and unexcited molecules that interact through forces of different types. The goal of this work is to develop some model interaction potentials between the excited and unexcited molecules. It is shown that the interaction between the excited particles is short-range and repulsive. The interaction between the excited and unexcited particles is long-range and can be either attractive or repulsive. Using the thermodynamic perturbation theory, a change in the chemical potential of excited particles with respect to that of unexcited ones is estimated.*

*Keywords:* intermolecular interaction, physics of liquids, radiation effect, thermodynamic properties.

### 1. Introduction

The properties of liquids are controlled by applying external factors to them, such as electric and magnetic fields, pressure, optical and particle irradiation [1–4]. If the properties of liquids or liquid systems change noticeably, when the external control

parameters change, then they are called smart liquids [5]. From the viewpoint of their applications, the study of those liquids, in turn, is the subject of such a promising science as microfluidics, that is, the physics of liquids in small volumes [3, 4].

Very often, the manipulation of the properties of liquid media is carried out by applying external factors not directly, but by changing some “intermediate” property. For example, to move the liquid through microscopic channels, the thermocapillary effect [6] is used, at which the surface tension coefficient changes under irradiation. In this case, it is believed that a change in the surface tension is caused by a local temperature growth. That is, the external field effect

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is reduced to the local dissipation of the energy of this field.

On the other hand, it is known that irradiation induces the appearance of a certain number of excited molecules. In this case, the nature of the potential of their interaction with unexcited molecules changes not only quantitatively, but also qualitatively: from attractive short-range (inversely proportional to the sixth power of the distance) to long-range (inversely proportional to the third power of the distance) one, which can be both attractive and repulsive [2, 7, 8]. The extent to which this fact can affect the properties of liquids and liquid systems, including thermophysical ones, remains unclear. If the effect of the interaction potential change turns out noticeable, then its application opens up prospects for a more subtle and intelligent way of manipulating the properties of molecular liquids, which, in turn, will become a basis for the development of new technologies in microrobotics and biotechnology.

In most works, the radiation effect on the properties of liquids and liquid systems, including molecular ones, is considered from two aspects:

1) the effect consisting in changing the chemical composition of the irradiated liquid (the issue mostly concerns the formation of free radicals and the dissociation of molecules into ions, i.e., what is called the phenomenon of radiolysis [9]);

2) the effect consisting in a local increase in the liquid temperature due to the radiation absorption, which leads to the appearance of a temperature gradient and the corresponding non-equilibrium processes [10–12].

However, some radiation effects on liquid systems are known today that cannot be explained by a change in the system composition or a local temperature growth. This concerns in particular an appreciable increase in the rate of evaporation of liquids, both pure, such as water [13, 14] or alcohols [14, 15], and solutions [16].

A more profound approach to the study of those phenomena, which is based on determining the change in the configurational entropy and the chemical potentials of the system components under irradiation, was developed in works [17, 18]. In particular, it was concluded that the radiation action leads to the excitation of molecules in various phases, which, in turn, leads to a decrease of the chemical potential value. As a result, the phase equilibrium in the

irradiated liquid systems changes, as well as the formation kinetics of a new phase. The key assumption in the framework of the proposed approach is the consideration of liquid systems as two-component solutions consisting of excited and unexcited molecules, which are regarded as different particles. The next logical step is the application of that or another solution model. The first approximation is the model of ideal solution, which is used to estimate the changes in the parameters of the coexistence curves between the liquid phase and various other phases, when such systems are irradiated.

Later, the model of regular solution was also analyzed [19]. However, the fact that the interaction potential between the excited and unexcited molecules has a qualitatively different nature than the interaction potential between the molecules in the ground electronic state contradicts the initial assumptions on the interaction origin that forms the basis for the statistical foundation of regular solution models, especially the ideal-solution model [20]. Therefore, there arises a necessity to study the models of solutions of excited and unexcited molecules with regard for the realistic potentials of their interaction and analyze the thermophysical properties of those systems.

## 2. Intermolecular Interaction Potential Model

Thus, we are faced with the task of developing and justifying the models of interaction between excited and unexcited particles. In other words, we have to propose interaction potentials between them, in order to subsequently use those potentials to calculate various thermophysical properties by applying the Monte Carlo or molecular dynamics method.

Let us firstly consider the interaction between unexcited particles. One of the most common models describing such an interaction is the model in which the interaction potential is given by the Lennard-Jones formula [2]:

$$\phi(r) = 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \quad (1)$$

where  $\sigma$  is the effective diameter of the atom,  $\varepsilon$  is an energy parameter, and  $r$  is the distance between the centers of interacting atoms. The functional form of the attractive part of this potential is theoretically justified on the basis of quantum mechanical perturbation theory. Let us compare it with the London

formula [7, 8] for the potential energy of dispersion interaction,

$$\phi(r) = -\frac{1}{(4\pi\epsilon_0)^2} \frac{3\hbar}{2} \alpha_1 \alpha_2 \frac{\omega_1 \omega_2}{\omega_1 + \omega_2} \frac{1}{r^6}. \quad (2)$$

Here,  $\alpha_1$  and  $\alpha_2$  are the polarizability coefficients of the molecules, and  $\omega_1$  and  $\omega_2$  are the transition frequencies. Note that the London formula is exact in the two-level case, i.e., if there are only the ground state and one excited state of the molecule. The polarizability coefficient  $\alpha$ —or, more exactly, the combination  $\alpha/(4\pi\epsilon_0)$ —has the dimension of  $\text{m}^3$  and is equal to the “effective volume” of the molecule by the order of magnitude. Thus, we can put the parameter  $\sigma$  from the Lennard-Jones potential (1) to be equal to

$$\sigma = \sqrt[3]{\frac{\alpha}{4\pi\epsilon_0}}, \quad (3)$$

or to

$$\sigma_{12} = \sqrt[6]{\frac{\alpha_1 \alpha_2}{(4\pi\epsilon_0)^2}}$$

if we are talking about the interaction between the molecules of different types. The energy parameter in the Lennard-Jones potential will be expressed as follows:

$$\varepsilon_{12} = \frac{3}{8} \frac{\hbar\omega_1\omega_2}{\omega_1 + \omega_2}.$$

If the set of energy levels is the same (which occurs in the case where the interaction between the excited and unexcited molecules is considered), then

$$\varepsilon = \frac{3}{8} \frac{\hbar\omega}{2}. \quad (4)$$

In order to find an expression for the interaction potential between excited and unexcited molecules, we used the results of the work by Bostrom and Ninham [21], where the following expression for the energy of dispersion interaction between excited and unexcited particles was obtained:

$$\phi(r) = \frac{1}{4\pi\epsilon_0} \frac{\hbar\omega}{2} \frac{\alpha}{\epsilon r^3} (3 \cos^2 \theta - 1). \quad (5)$$

Here,  $\theta$  is the angle between the direction of the transition dipole moment of the molecule  $\langle 1|\hat{\mathbf{d}}|0\rangle$  and the line that connects the excited and unexcited

molecules, and  $\langle 1|$  and  $|0\rangle$  are the excited and ground states of the molecule, respectively.

Using the relationship of the Lennard-Jones potential parameters  $\sigma$  and  $\varepsilon$  with the transition frequency to the excited level  $\omega$  and the polarizability coefficient  $\alpha$  [Eqs. (3) and (4), respectively], we can write the following expression for the dispersion energy (5):

$$\phi(r) = \sigma^3 \frac{8\varepsilon}{3\epsilon} \frac{(3 \cos^2 \theta - 1)}{r^3}.$$

Finally, we obtain the following expression for the interaction potential between the excited and unexcited molecules:

$$\phi(r) = 4\varepsilon \left(\frac{\sigma}{r}\right)^{12} + 4\varepsilon C \left(\frac{\sigma}{r}\right)^3 (3 \cos^2 \theta - 1), \quad (6)$$

where  $C = 2/(3\epsilon)$ . In our opinion, it is pertinent to consider the constant  $C$  as a fitting parameter of the model.

In order to find an expression for the interaction potential between the excited molecules  $a$  and  $b$ , we considered the expression for the dispersion energy as a second-order correction to the energy in the framework of the quantum mechanical perturbation theory,

$$\Delta E_{kl} = -\frac{1}{(4\pi\epsilon_0)^2} \frac{1}{r^6} \times \sum_{m,n \neq k,l} \frac{|\langle k|\hat{\mathbf{d}}_a|m\rangle|^2 |\langle l|\hat{\mathbf{d}}_b|n\rangle|^2}{(E_m^a - E_k^a) + (E_n^b - E_l^b)}.$$

If all levels are neglected except for the ground and the first excited one, i.e., the two-level model is considered, then the corresponding corrections for the energies of those two states will be identical in magnitude but different in sign. Really,

$$\begin{aligned} \Delta E_{00} &= -\frac{1}{(4\pi\epsilon_0)^2} \frac{1}{r^6} \frac{|\langle 0|\hat{\mathbf{d}}_a|1\rangle|^2 |\langle 0|\hat{\mathbf{d}}_b|1\rangle|^2}{(E_1^a - E_0^a) + (E_1^b - E_0^b)} = \\ &= \frac{|\langle 0|\hat{\mathbf{d}}_a|1\rangle|^2 |\langle 0|\hat{\mathbf{d}}_b|1\rangle|^2}{(E_0^a - E_1^a) + (E_0^b - E_1^b)} = -\Delta E_{11}. \end{aligned}$$

Therefore, we can conclude that the dispersion interaction between the excited molecules has a repulsive character. This fact makes it possible to write the interaction potential between the excited molecules in the form

$$\phi(r) = 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{12} + \left(\frac{\sigma}{r}\right)^6 \right]. \quad (7)$$

### 3. Thermodynamic Perturbation Theory

Let us write down the Hamiltonian of the system of excited and unexcited particles,

$$H = \sum_{i=1}^{N_g} \frac{\mathbf{P}_i^{g2}}{2m_g} + \sum_{k=1}^{N_e} \frac{\mathbf{P}_k^{e2}}{2m_e} + U(\mathbf{x}_1^g, \dots, \mathbf{x}_{N_e}^e), \quad (8)$$

where  $N_g$  and  $N_e$  are the numbers of unexcited and excited particles, respectively,  $\mathbf{P}_i^g$  and  $\mathbf{P}_k^e$  are the momenta of the  $i$ -th unexcited and  $k$ -th excited particles, respectively, and  $\mathbf{x}_i \equiv (\mathbf{r}_i, \boldsymbol{\Omega}_i)$  is the set of generalized coordinates of the  $i$ -th particle, which includes the coordinates  $\mathbf{r}_i$  of the center of mass of this particle and the angles  $\boldsymbol{\Omega}_i$  that define the particle orientation. The orientation of an excited particle is given by the orientation of the instantaneous transient dipole moment. The masses of unexcited,  $m_g$ , and excited,  $m_e$ , molecules are assumed to be identical,  $m_g = m_e = m$ . The potential energy  $U$  of the system in the pair-interaction approximation can be written as follows:

$$U = \sum_{i<j}^{N_g} \phi_{ij}^{gg} + \sum_{k<l}^{N_e} \phi_{kl}^{ee} + \sum_{i=1}^{N_g} \sum_{k=1}^{N_e} \phi_{ik}^{ge}, \quad (9)$$

where the pairwise interaction potentials between the unexcited,  $\phi^{gg}$ , excited,  $\phi^{ee}$ , and excited and unexcited,  $\phi^{ge}$ , molecules are given by expressions (1), (7), and (6), respectively.

Since the interaction potentials between the excited particles and between the excited and unexcited particles do not differ at small distances from the interaction potential between the unexcited particles (they all have the same repulsive component, which tends to infinity as  $r^{-12}$  at  $r \rightarrow 0$ ; see Eqs. (6) and (7)), the corresponding potentials can be represented as some perturbations with respect to the interaction potential between the unexcited particles, i.e.,

$$\phi^{ge}(\mathbf{x}_i, \mathbf{x}_j; \lambda) = \phi^{gg}(r_{ij}) + \lambda v(\mathbf{x}_i, \mathbf{x}_j), \quad (10)$$

$$\phi^{ee}(\mathbf{x}_i, \mathbf{x}_j; \mu) = \phi^{gg}(r_{ij}) + \mu w(\mathbf{x}_i, \mathbf{x}_j), \quad (11)$$

where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ , and  $\lambda$  and  $\mu$  are parameters that “regulate the switching” of the corresponding perturbation. If  $\lambda = 0$  and  $\mu = 0$ , we have an unperturbed system consisting only of unexcited particles; at  $\lambda = 1$  and  $\mu = 1$ , expression (10) coincides with the interaction potential (6) between the excited and unexcited

particles, and expression (11) with the interaction potential (7) between the excited particles. Thus, the expressions for  $v$  and  $w$  can be written in the following forms:

$$v(\mathbf{x}_i, \mathbf{x}_j) = 4\varepsilon \left(\frac{\sigma}{r}\right)^6 + 4\varepsilon C \left(\frac{\sigma}{r}\right)^3 (3 \cos^2 \theta - 1), \quad (12)$$

$$w(\mathbf{x}_i, \mathbf{x}_j) = 8\varepsilon \left(\frac{\sigma}{r}\right)^6, \quad (13)$$

where  $r \equiv r_{ij}$ . Now the potential energy of the system can be represented as the sum of the potential energy  $U_0$  of the unperturbed system consisting of only unexcited particles and the perturbation that arises due to the modification of the pair-interaction potentials between the excited particles, i.e.,

$$U = U_0 + \lambda V + \mu W, \quad (14)$$

where

$$U_0 = \sum_{i<j}^N \phi_{ij}^{gg}, \quad V = \sum_{i=1}^{N_g} \sum_{k=1}^{N_e} v_{ik}^{ge}, \quad dW = \sum_{k<l}^{N_e} \phi_{kl}^{ee}, \quad (15)$$

and  $N = N_g + N_e$  denotes the total number of particles.

The free energy  $F$  of the perturbed system looks like

$$F = F_{id} - k_B T \ln Q \quad (\lambda = 1, \mu = 1), \quad (16)$$

where

$$Q(\lambda, \mu) = \int d\mathbf{x}_1^g \dots d\mathbf{x}_{N_e}^e \exp\left(-\frac{U(\lambda, \mu)}{k_B T}\right)$$

is the configurational statistical sum with the gradual “switching on” of the perturbation,  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $F_{id}$  is the part of the free energy that arises as a result of integration over the particle momenta in the statistical sum [22],

$$\frac{F_{id}}{k_B T} = -N_g \ln \left(\frac{z_g^e}{N_g \lambda_g^3}\right) - N_e \ln \left(\frac{z_e^e}{N_e \lambda_e^3}\right). \quad (17)$$

Here,  $z_g$  and  $z_e$  are the statistical sums over the internal degrees of freedom of the unexcited and excited molecules, respectively, and  $\lambda_g$  and  $\lambda_e$  are the corresponding de Broglie wavelengths. In what follows, we assume that  $z_g = z_e = z$  and  $\lambda_g = \lambda_e = \lambda$ .

The free energy  $F$  of the perturbed system can be expressed in terms of the parameters of unperturbed

system by expanding  $F(\lambda, \mu)$  in a series of  $\lambda$  and  $\mu$ , and putting  $\lambda = \mu = 1$ . Up to linear terms, we obtain [22]

$$F = F_0 + \langle V \rangle_0 + \langle W \rangle_0, \quad (18)$$

where

$$F_0 = F_{id} - k_B T \ln Q_0, \quad (19)$$

$\langle \dots \rangle_0$  denotes averaging over the unperturbed configuration distribution function, and  $Q_0 \equiv Q(\lambda = 0, \mu = 0)$ . The average values of the perturbation energy are expressed using the two-particle distribution functions  $n_2^{ge}$  and  $n_2^{ee}$  [22],

$$\langle W \rangle_0 = \frac{1}{2} \int d\mathbf{x}_1^e d\mathbf{x}_2^e w(\mathbf{x}_1^e, \mathbf{x}_2^e) n_2^{ee}(\mathbf{x}_1^e, \mathbf{x}_2^e), \quad (20)$$

$$\langle V \rangle_0 = \int d\mathbf{x}_1^g d\mathbf{x}_1^e v(\mathbf{x}_1^g, \mathbf{x}_1^e) n_2^{ge}(\mathbf{x}_1^g, \mathbf{x}_1^e), \quad (21)$$

where

$$n_2^{ee}(\mathbf{x}_1^e, \mathbf{x}_2^e) = N_e(N_e - 1) \int' d\mathbf{x}_1^g \dots d\mathbf{x}_{N_e}^e \frac{e^{-\frac{U_0}{k_B T}}}{Q_0}, \quad (22)$$

$$n_2^{ge}(\mathbf{x}_1^g, \mathbf{x}_1^e) = N_g N_e \int' d\mathbf{x}_1^g \dots d\mathbf{x}_{N_e}^e \frac{e^{-\frac{U_0}{k_B T}}}{Q_0}. \quad (23)$$

The primed integrals in formulas (22) and (23) mean that integration is not performed over the variables  $\mathbf{x}_1^e$  and  $\mathbf{x}_2^e$  in the former, and over the variables  $\mathbf{x}_1^g$  and  $\mathbf{x}_1^e$  in the latter. Formulas (20) and (21) can be simplified further by using the fact that the function  $w$  depends only on  $r_{12}^{ee}$ , and the function  $v$  depends on  $\mathbf{r}_{11}^{ge}$ ,  $\mathbf{\Omega}_1^g$ , and  $\mathbf{\Omega}_1^e$ . So, we have

$$\begin{aligned} \langle W \rangle_0 &= \frac{1}{2} \int \int d\mathbf{r}_1^e d\mathbf{r}_2^e w(r_{12}^{ee}) \rho_2^{ee}(\mathbf{r}_1^e, \mathbf{r}_2^e) = \\ &= \frac{\mathcal{V} \rho_e^2}{2} \int d\mathbf{r}_{12}^{ee} w(r_{12}^{ee}) g_2^{ee}(r_{12}^{ee}) = \frac{\mathcal{V} \rho_e^2}{2} \langle w \rangle, \end{aligned} \quad (24)$$

where  $\mathcal{V}$  is the system volume,  $\rho_e = N_e/\mathcal{V}$  is the concentration of excited particles, and  $\langle w \rangle$  is the corresponding integral. Here we have used the fact that the relationship between the two-particle,  $n_2$ , and the coordinate two-particle,  $\rho_2$ , distribution functions in a homogeneous and isotropic system is as follows:

$$n_2(\mathbf{x}_1, \mathbf{x}_2) = (4\pi)^{-2} r_2(\mathbf{r}_1, \mathbf{r}_2) = (4\pi)^{-2} \rho^2 g_2(r_{12}),$$

where  $g_2$  is the radial distribution function [22].

Next,

$$\langle V \rangle_0 = \frac{\rho_g \rho_e}{(4\pi)^2} \int d\mathbf{x}_1^g d\mathbf{x}_1^e v(\mathbf{r}_{11}^{ge}, \mathbf{\Omega}_1^g, \mathbf{\Omega}_1^e) g_2^{ge}(r_{11}^{ge}). \quad (25)$$

In order to distinguish the orientational part, it is convenient to represent the perturbation potential as the sum of two terms,

$$v = v_i(r_{11}^{ge}) + v_a(r_{11}^{ge}) P_2(\cos \theta).$$

Here,  $P_2(\cos \theta)$  is the second-degree Legendre polynomial, and  $v_i$  and  $v_a$  are given by the expressions

$$v_i(r) = 4\varepsilon \left(\frac{\sigma}{r}\right)^6, \quad v_a(r) = 8\varepsilon C \left(\frac{\sigma}{r}\right)^3. \quad (26)$$

Using the formula for the summation of spherical functions [22], the orientational part of the excitation potential can be represented in the following form:

$$P_2(\cos \theta) = \frac{4\pi}{2 \cdot 2 + 1} \sum_{m=-2}^2 Y_{2m}(\mathbf{\Omega}) Y_{2m}^*(\mathbf{\Omega}^e),$$

where  $\mathbf{\Omega}$  are the orientation angles of the vector connecting the centers of two particles. Changing to new variables  $\mathbf{r}_{11}^{ge} = \mathbf{r}_1^g - \mathbf{r}_1^e$  and  $\mathbf{R} = (\mathbf{r}_1^g + \mathbf{r}_1^e)/2$  and integrating over  $\mathbf{R}$  and  $\mathbf{\Omega}$ , we obtain

$$\langle V \rangle_0 = \mathcal{V} \rho_e \rho_g \int d\mathbf{r}_{11}^{ge} g_2^{ge}(r_{11}^{ge}) v_i(r_{11}^{ge}) = \mathcal{V} \rho_e \rho_g \langle v \rangle. \quad (27)$$

Using expressions (17)–(19), (24), and (27), we can find the chemical potentials for excited,  $\mu_e$ , and unexcited,  $\mu_g$ , particles:

$$\mu_g = \frac{\partial F}{\partial N_g} = \mu_g^\circ + k_B T \ln \rho_g + \mu_g^{ex} + \rho_e \langle v \rangle, \quad (28)$$

$$\mu_e = \frac{\partial F}{\partial N_e} = \mu_e^\circ + k_B T \ln \rho_e + \mu_e^{ex} + \rho_g \langle v \rangle + \rho_e \langle w \rangle, \quad (29)$$

where

$$\mu_g^\circ = -k_B T \ln \frac{z_g}{\lambda_g^3}, \quad \mu_e^\circ = -k_B T \ln \frac{z_e}{\lambda_e^3}$$

are the chemical potentials of excited and unexcited particles, respectively, in the “standard state” ( $\rho = 1$ ), and

$$\frac{\mu_g^{ex}}{k_B T} = \frac{\partial}{\partial N_g} \ln \frac{Q_0}{V^{N_g + N_e}} = \ln \frac{Q_0(N_g + 1, N_e)}{V Q_0(N_g, N_e)}, \quad (30)$$

$$\frac{\mu_e^{ex}}{k_B T} = \frac{\partial}{\partial N_e} \ln \frac{Q_0}{V^{N_g + N_e}} = \ln \frac{Q_0(N_g, N_e + 1)}{V Q_0(N_g, N_e)} \quad (31)$$

are the excess parts of the chemical potential, i.e., those parts of the work required to “create” particles in the system that arises as a result of interaction between the particles. The partial derivatives in formulas (28)–(31) are calculated provided that the system volume  $\mathcal{V}$ , temperature  $T$ , and the number of particles of the “opposite” type,  $N_e$  or  $N_g$ , are constant. If the rotational, vibrational, and electronic statistical sums of the molecule in the ground and excited states are assumed to remain constant, then the chemical potentials  $\mu_g^\circ$  and  $\mu_e^\circ$  in the “standard states” can also be considered identical. The excess parts of the chemical potentials  $\mu_g^{ex}$  and  $\mu_e^{ex}$  are also identical because the interaction between the particles of both types in the unperturbed state is identical. Thus, the difference between the chemical potentials of an excited and an unexcited particle,  $\Delta\mu = \mu_e - \mu_g$ , is equal to

$$\Delta\mu = k_B T \ln \frac{\rho_e}{\rho_g} + (\rho_e - \rho_g)\langle v \rangle + \rho_e \langle w \rangle. \quad (32)$$

If the number of excited particles is much smaller than the number of unexcited ones,  $N_e \ll N_g \approx N$ , then expression (32) can be simplified,

$$\frac{\Delta\mu}{k_B T} = \ln x_e - \frac{\rho \langle v \rangle}{k_B T}, \quad (33)$$

where  $x_e = N_e/N_g \approx N_e/N$  is the mole fraction of excited particles. The first term on the right-hand side of Eq. (33) is the “ideal solution” term, which arises due to the formation of particles of a new type, and the second term characterizes the change of the chemical potential due to the change in the interaction potential between the molecules.

#### 4. Conclusions

In this work, the model potentials are proposed for the interaction between excited and unexcited particles and between excited particles. The interaction between excited particles is short-range and has a repulsive character. The interaction between excited and unexcited particles is long-range and can have both attractive and repulsive characters. Considering the irradiated liquid as a set of unexcited and excited molecules and using the thermodynamic theory of perturbation in the linear approximation, an expression for the change of the chemical potential of a molecule at its excitation is derived. At low irradiation doses (corresponding to low concentrations of

excited particles), the difference between the chemical potentials of the excited and unexcited particles includes two terms: the ideal-solvent term and the term arising from the change of the intermolecular interaction potential.

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#### ВПЛИВ ВИПРОМІНЮВАННЯ НА ХІМІЧНИЙ ПОТЕНЦІАЛ МОДЕЛЬНИХ РІДИН

Опромінення, зокрема радіаційне, є одним з чинників впливу на молекулярні механізми фізіологічних процесів в людському організмі. Здебільшого цей вплив проявляється в зміні хімічного складу або локальному нагріванні, що виводить систему з рівноважного стану. Сучасні підходи до вивчення цих ефектів базуються на моделюванні змін конфігураційної ентропії й хімічних потенціалів рідин у процесі опромінення. У межах такого підходу рідина розглядається як двокомпонентний розчин збуджених і незбуджених молекул, які мають різні типи взаємодії. Метою роботи була розробка модельних потенціалів взаємодії між збудженими й незбудженими молекулами. Показано, що взаємодія між збудженими частинками є короткодіючою й має характер відштовхування. Взаємодія між збудженою і незбудженою частинками є далекодіючою й може мати характер як притягання, так і відштовхування. За допомогою термодинамічної теорії збурень було оцінено зміну хімічного потенціалу збудженої частинки відносно незбудженої.

*Ключові слова:* міжмолекулярна взаємодія, фізика рідин, вплив опромінення на термодинамічні властивості.