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## PHYSICAL NATURE OF RELAXATION TIME IN AQUEOUS ALCOHOLIC SOLUTIONS

*The kinetics of relaxation processes in aqueous alcoholic solutions has been studied. A model for the nonequilibrium state of those solutions is proposed, in which the slowest relaxation process is associated with the destruction of new phase nuclei. The process of their destruction is described in the framework of both the Lagrangian formalism with low dissipation and the nucleation theory. The self-diffusion coefficients of molecules from the nucleus surface are calculated and used to estimate the lifetime of nuclei and its dependence on the nucleus size. A relation between the diffusion coefficient of nuclei in the nucleus-size space and the coefficient of molecular self-diffusion from the nucleus surface is found. A comparison with available experimental data is made.*

*Keywords:* relaxation kinetics, aqueous alcoholic solution, formation of new-phase nuclei, dissipation of new-phase nuclei, self-diffusion coefficient of molecules from the nucleus surface.

### 1. Introduction

Researches of the dynamic light scattering in aqueous glycerol solutions [1–5] showed that an equilibrium state is reached in them in a period of one to two weeks. A similar result was obtained earlier in work [6], when studying the intensity of molecular light scattering in alcoholic electrolyte solutions. In work [7], using the correlation spectroscopy methods, the characteristic size of microscopic inhomogeneities,  $r$ , and the characteristic time of the fluctuation damping,  $\tau$ , were determined. It was shown that  $r \sim 10^{-4}$  cm and  $\tau \sim 10^{-3}$  s in aqueous ethyl alcohol solutions. The application of the correlation spectroscopy, while researching aqueous solutions of tert-butyl alcohol [8], testified that the time evolution of fluctuations is determined by two characteristic relaxation times:  $\tau_1 \sim 10^{-5}$  s and  $\tau_2 \sim 10^{-2}$  s. The former corresponds to the relaxation owing to the diffusion processes in a solution. The latter relaxation time has not been interpreted properly till now.

The physical nature of relaxation processes in aqueous alcoholic solutions was discussed in work [9]. In the cited review, by analyzing a large body of experimental results, it was demonstrated that there are regularities that can be adequately explained in the framework of the hypothesis about a microscopically

non-uniform solution structure [9–12]. This hypothesis is confirmed by (i) some features in the scattering of light that passes through aqueous alcoholic solutions, (ii) a reduction in the intensity of molecular light scattering, when the solution approaches its equilibrium state, and (iii) the character of the angular asymmetry of light scattering.

All available facts allow us to draw a conclusion about the generation of nuclei of a metastable phase in the equilibrium phase. The destruction of those nuclei occurs owing to the molecular diffusion from their surface. This process is slow and depends on the nucleus size. From whence, it follows that a detailed theoretical study of the evolution of nuclei governed by the diffusion of the substance from their surface becomes challenging. This was the aim of this work. Here, the self-diffusion coefficient of molecules from the nucleus surface is calculated, and the dependence of the nucleus lifetime on the nucleus size is estimated. A careful comparison with experimental data is made.

### 2. Evolution Kinetics of New-Phase Nuclei in Aqueous Alcoholic Solutions

According to works [1–8], which were discussed above, nuclei of a metastable phase are formed in aqueous alcoholic solutions. A continuous formation and destruction of nuclei in the solutions takes place at

that. In this work, only the process of nucleus destruction will be considered. This process is supposed to be governed by the following mechanism. Because of thermal fluctuations, the initial spherical surface of a nucleus slightly changes its shape. The resulting weakly non-spherical surface does not completely relax into its original state, which is impeded by the energy consumption to overcome viscous effects. A piece of the substance that could be detached from the initially spherical nucleus becomes more and more captured by hydrodynamic flows in the course of next surface fluctuations and moves away from the nucleus surface. The direct diffusion of molecules from the nucleus surface gives rise to a significantly slower process of nucleus destruction.

Below, we develop a simple model that implements the described mechanism of nucleus destruction. Let a deviation of the nucleus surface from the initially spherical shape be characterized by the radius  $r_s$ ,

$$r_s = r_0 + \delta r(\theta, \alpha), \quad |\delta r(\theta, \alpha)| \ll r_0, \quad (1)$$

where  $r_0$  is the radius of the spherical nucleus. It is natural to expand the function  $\delta r(\theta, \alpha)$  in a series in the spherical functions  $Y_{mn}(\theta, \alpha)$ ,

$$\delta r(\theta, \alpha) = \sum_{mn} \lambda_{mn} Y_{mn}(\theta, \alpha). \quad (2)$$

The expansion coefficients  $\lambda_{mn}$  and their time derivatives  $\dot{\lambda}_{mn}$  will be used below as generalized coordinates and velocities in the Lagrange function  $L = L(\lambda_{mn}, \dot{\lambda}_{mn}, t)$ . In order to take the viscous effects into account, let us introduce a dissipation function  $R = R(\lambda_{mn}, \dot{\lambda}_{mn}, t)$ . The corresponding Lagrange equation looks like

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\lambda}_{mn}} - \frac{\partial L}{\partial \lambda_{mn}} = \frac{\partial R}{\partial \dot{\lambda}_{mn}}. \quad (3)$$

The kinetic energy entering the Lagrange function is the sum of the contributions created by hydrodynamic flows inside and outside the nucleus surface:

$$T = \frac{1}{2} \int_{V_{\text{int}}} \rho \mathbf{v}^2 dV + \frac{1}{2} \int_{V_{\text{ext}}} \rho_n \mathbf{v}_n^2 dV, \quad (4)$$

where  $V_{\text{int}}$  and  $V_{\text{ext}}$  mean the respective regions, and  $\rho_n$  and  $\rho$  are the densities of the nucleus and the solution, respectively.

While determining the field of velocities  $\mathbf{v}_{\text{int}}$  and  $\mathbf{v}_{\text{ext}}$ , we assume that the nucleus can be regarded as a droplet of the incompressible fluid. In this case, the velocity field has a potential character, i.e.  $\mathbf{v} = -\text{grad } \varphi$ , and the potential  $\varphi$  satisfies the Laplace equations

$$\begin{aligned} \Delta \varphi_{\text{ext}} &= 0, \quad \text{for } r > r_s, \\ \Delta \varphi_{\text{int}} &= 0, \quad \text{for } r < r_s, \end{aligned} \quad (5)$$

and the boundary conditions

$$\begin{aligned} \varphi_{\text{ext}}(r_s) &= \varphi_{\text{int}}(r_s), \\ \frac{\partial \varphi_{\text{ext}}}{\partial r} \Big|_{r=r_s} &= \frac{\partial \varphi_{\text{int}}}{\partial r} \Big|_{r=r_s}. \end{aligned} \quad (6)$$

By substituting the corresponding expressions for the nucleus potentials  $\varphi_{\text{int}}$  and  $\varphi_{\text{ext}}$  [8], it is easy to be convinced that the kinetic energy of the system “nucleus–solution” is described by the expression

$$T = \frac{1}{2} r_0^3 \sum_{mn} \left( \frac{\rho}{\rho_n} + \frac{\rho}{\rho_{n+1}} \right) |\dot{\lambda}_{mn}|^2. \quad (7)$$

The potential energy in the Lagrange function is associated with the presence of the surface tension with the coefficient  $\sigma$  at the nucleus surface,

$$U = \sigma \delta S, \quad (8)$$

where  $\delta S$  is an increment of the nucleus surface area due to a surface deformation. It is easy to be convinced that the potential energy of the nucleus equals

$$U = \frac{1}{2} \sigma \sum_{mn} (n-1)(n+2) |\dot{\lambda}_{mn}|^2. \quad (9)$$

Dissipative forces arise at the destruction of a nucleus owing to the viscous friction. In accordance with work [13], the required expression for the dissipation function  $R$  in the case of incompressible fluid looks like

$$\begin{aligned} R &= \frac{\eta_n}{2} \int_{V_{\text{int}}} \left( \frac{\partial v_i^{(1)}}{\partial x_k} + \frac{\partial v_k^{(1)}}{\partial x_i} \right)^2 dV + \\ &+ \frac{\eta}{2} \int_{V_{\text{ext}}} \left( \frac{\partial v_i^{(2)}}{\partial x_k} + \frac{\partial v_k^{(2)}}{\partial x_i} \right)^2 dV. \end{aligned} \quad (10)$$

In view of the formula for the components of velocities expressed in terms of the derivatives of velocity potentials [14], we obtain

$$R = 2r_0 \sum_{mn} [\eta(n+2) + \eta_n(n-1)] \left| \dot{\lambda}_{mn} \right|^2, \quad (11)$$

where  $\eta$  and  $\eta_n$  are the shear viscosity coefficients for the solution and the nucleus, respectively.

The Lagrange equation for the variable  $\lambda_{mn}$  has the form

$$\ddot{\lambda}_{mn} + \frac{1}{\tau_n} \dot{\lambda}_{mn} + \omega_n^2 \lambda_{mn} = 0. \quad (12)$$

Here,

$$\omega_n = \omega_0 \sqrt{(n^2 - 1)(n + 2)}$$

is the frequency of the  $n$ -th ( $n \neq 0$ ) oscillation mode,

$$\omega_0 = \frac{\sigma}{r_0^3 (\rho_1 + \rho_2)}$$

is the frequency of undamped oscillations in the initial oscillatory mode,

$$\tau_n = \frac{\tau_0}{n^2}$$

is the relaxation time for the  $n$ -th ( $n \neq 0$ ) oscillation mode, and

$$\tau_0 = \frac{r_0^2 (\rho + \rho_n)}{2(\eta + \eta_n)}$$

is the relaxation time for the initial oscillatory mode.

The solution of Eq. (12) that satisfies the initial conditions reads

$$\lambda_{mn}(t) = \lambda_{mn}(0) e^{-\frac{t}{2\tau_n}} \cos \omega_n t. \quad (13)$$

### 3. Autocorrelation Function for the Shifts of Surface Points and the Self-Diffusion Coefficient

While finding the self-diffusion coefficient for molecules from the nucleus surface, we used the temporal correlation function for the radial velocity component of the points at the surface:

$$D_s = \int_0^\infty \langle v_r(t), v_r(0) \rangle dt.$$

By substituting  $v_{int}$  for  $v_r$  in this formula and using the expression

$$\langle |\lambda_{mn}(0)|^2 \rangle = \frac{k_B T}{\sigma(n-1)(n+2)}$$

for fluctuations in the equilibrium state, we obtain

$$D_s \approx \frac{\kappa}{3} D_0, \quad D_0 = \frac{2k_B T (\eta + \eta_n)}{\sigma r_0^2 (\rho + \rho_n)}, \quad (14)$$

where  $k_B$  is the Boltzmann constant, and

$$\kappa = \sum_{n=0}^{n_{\max}} \frac{1}{n^4}. \quad (15)$$

The number of terms in sum (15) is bounded ( $n \leq n_{\max}$ ), because we only consider those of them, for which the distance between two neighbor deviation maxima exceeds the size of molecules  $a$  ( $\lambda_n \gg a$ ). Since  $\lambda_n \sim \frac{2\pi r}{n}$ , we obtain that  $n_{\max} = \frac{2\pi r}{a}$ .

It is also evident that the equilibration time depends on the nucleus size. We assume that the nucleus is destroyed only due to irreversible surface oscillations of its shape. Then its lifetime  $\tau_l$  can be estimated by the formula

$$\tau_l \sim \frac{r^2}{4D_s}, \quad (16)$$

or

$$\tau_l \sim \frac{3r^2}{2\kappa D_0}. \quad (17)$$

Now, let us discuss the typical values of all parameters entering formulas (16) and (17). In accordance with works [6–8], a characteristic size  $r$  of a nucleus in aqueous ethanol solutions is of an order of  $r \sim 10^{-4}$  cm. The size of an ethanol molecule amounts to  $a \approx 4.5 \times 10^{-8}$  cm. Therefore,  $n_{\max} = 6 \times 10^4$  and  $\kappa \approx 1$ . The surface tension coefficient  $\sigma$  for a nucleus with the bulk properties close to those in the surrounding solution satisfies the inequalities  $\sigma \ll (\sigma_W, \sigma_{Et})$ , where  $\sigma_W$  and  $\sigma_{Et}$  are the surface tension coefficients for water and ethanol, respectively. This fact enables us to adopt the estimate  $\sigma \sim 10$  erg/cm<sup>2</sup>. For the same reason, the values of  $\eta$  and  $\eta_n$  should also be close to each other. We take that  $(\eta, \eta_n) \sim 10^{-3}$  g/(cm s). Assuming that  $\rho \sim 1$  g/cm<sup>3</sup>, we obtain the following estimate:  $D_0 \sim 10^{-8}$  cm<sup>2</sup>/s.

The values obtained for the self-diffusion coefficients of molecules and the destruction times for

nuclei with various dimensions are quoted in Table 1. Let us discuss the results of calculations. According to works [3–8], the relaxation time  $\tau$  for fluctuation processes in aqueous alcoholic solutions has an order of  $10^{-3} \div 10^{-5}$  s. Therefore, from the presented theory, it follows that the optimum nucleus size amounts to  $r \sim 10^{-5} \div 10^{-4}$  cm.

#### 4. Comparison Between the Results Obtained and the Nucleation Theory

In this section, the results obtained are compared with the results of the standard nucleation theory [14–16]. First of all, the matter concerns the comparison between the nucleus destruction times.

In accordance with works [14–16], the size distribution function of nuclei,  $f(r, t)$ , satisfies the equation

$$\frac{\partial f(r, t)}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 J_r), \quad (18)$$

where

$$J_r = -D(r) \left[ \frac{\partial f(r, t)}{\partial r} + \frac{\Delta\Phi'(r)}{k_B T} f(r, t) \right]$$

is the flow density in the nucleus-size space,  $D(r)$  the corresponding diffusion coefficient, and  $\Delta\Phi$  the variation of the thermodynamic potential of the system when a nucleus emerges. This potential looks like

$$\Delta\Phi(r) = 4\pi r^2 \sigma - \frac{8\pi r^3 \sigma}{3r^*}, \quad (19)$$

where  $r^*$  is the critical nucleus radius. In a vicinity of the thermodynamic potential maximum, the stationary distribution function looks like

$$f_0(r) = f_0(r^*) \exp \left[ \frac{4\pi\sigma}{k_B T} (r - r^*)^2 \right], \quad (20)$$

where

$$f_0(r^*) \approx \exp \left( \frac{-4\pi\sigma r^{*2}}{3k_B T} \right)$$

**Table 1. Results of theoretical calculations of the self-diffusion coefficient and the destruction time for nuclei with various sizes**

$r$ , cm	$10^{-3}$	$10^{-4}$	$10^{-5}$
$D_s$ , cm/s	$10^{-10}$	$10^{-8}$	$10^{-6}$
$\tau_l$ , s	$10^2$	$10^{-2}$	$10^{-6}$

is the size distribution function of nuclei at the critical point.

In order to determine the character of the nucleus size variation in time, let us make the following simplifications: 1)  $\Delta(r^*) < (\text{or } \ll) k_B T$ , because, according to experimental results [8], the processes of nucleus emergence and destruction in the system take place permanently; and 2) the diffusion coefficient weakly depends on the nucleus dimensions. In this case, the distribution function, which satisfies the boundary conditions

$$\begin{aligned} f(r, 0) &= \delta(r - r_0), \\ f(r, \infty) &= 0, \end{aligned}$$

where  $r_0$  is the initial size of a new-phase nucleus, looks like

$$f(r, t) = \frac{1}{\sqrt{4\pi D_0 t}} \left( e^{-\frac{(r-r_0)^2}{4Dt}} + e^{-\frac{(r+r_0)^2}{4Dt}} \right). \quad (21)$$

Note that it is a solution of the diffusion equation on the semiaxis  $r > 0$ . The average nucleus size is evaluated in the standard way and equals

$$r(t) = r_0 \left[ 1 - e^{-\frac{\tau_l}{t}} \right], \quad (22)$$

where

$$\tau_l \approx \frac{r_0^2}{4D} \quad (23)$$

is the nucleus lifetime, and  $D$  the diffusion coefficient in the nucleus-size space. According to work [11], this parameter equals

$$D = \frac{k_B T}{\eta r_0}. \quad (24)$$

One can see that it has the same dependence on the shear viscosity and nucleus size as the self-diffusion coefficient for a Brownian particle. In other words, the coefficient of the diffusion-driven decrease of the nucleus radius coincides with the coefficient of the translational particle diffusion. This result is not quite clear. Moreover, the diffusion coefficient of the substance from the nucleus surface should be higher for the larger ratio between the thermal ( $\sim k_B T$ ) and surface tension ( $\sim \sigma r_0^2$ ) energies of the nucleus. In the limiting case  $\frac{k_B T}{\sigma r_0^2} \rightarrow 0$ , the diffusion from the nucleus surface should tend to zero (in this case, nucleus oscillations are not accompanied by the substance transfer). The same can be said about the dependence of the self-diffusion coefficient on the shear viscosity.

### 5. Discussion of the Results Obtained

In the sections above, we considered a model for the evolution of nonequilibrium states in aqueous alcoholic solutions, in which the slow equilibration in the solutions is associated with the destruction of nuclei of a new phase. The nuclei are destroyed owing to irreversible fluctuations in the nucleus surface shape. More specifically, the surface that acquired a random shape owing to fluctuations tends to restore its initial spherical form under the action of the surface tension forces. However, because of the viscosity, the initial surface is not restored completely, since some pieces of the nucleus substance migrate from the nucleus into the solution bulk. This process is described in the framework of the Lagrange formalism, which allows both the oscillations of the nucleus surface shape and the processes of fluctuation damping by viscous effects to be taken into account.

The proposed scenario of the nucleus evolution agrees satisfactorily with experimental data. Using the methods of dynamic light scattering [4, 5, 8] and ultrasonic spectroscopy [18, 19], we found that radial oscillations of nuclei give rise to the emergence of a peak in the ultrasound absorption. The frequency that characterizes the peak position agrees satisfactorily with the frequencies of nucleus surface oscillations. Really, according to our estimates, the fundamental frequency of nucleus surface oscillations, as well as hydrodynamic motions in the nucleus bulk, is equal to

$$\omega_0 = \sqrt{\frac{\sigma}{r_0^3(\rho + \rho_n)}} \sim 10^7 \text{ Hz}$$

for a nucleus with  $r \sim 10^{-5}$  cm. For nuclei with other sizes, the  $\omega_0$ -values are quoted in Table 2.

The existence of oscillatory processes in aqueous solutions of 2-propyl alcohols was studied in experimental work [18]. It was found that, at frequencies  $\omega \sim 10^7 \div 10^8$  Hz, the ultrasonic absorption peak takes place, which corresponds to the cluster sizes  $\xi \sim 10^{-5} \div 10^{-4}$  cm. The origin of this peak can

Table 2. Fundamental oscillation frequency for nuclei with various radii

$r$ , cm	$10^{-3}$	$10^{-4}$	$10^{-5}$
$\omega_0$ , Hz	$10^6$	$3 \times 10^6$	$10^7$

be associated with nucleus oscillations, as well as with the characteristic frequencies of clustering processes. Hence, it was shown that the optimum size of nuclei amounts to  $r \sim 10^{-5}$  cm.

This result agrees well with the correlation spectroscopy and molecular light scattering data [3–6]. In the cited works, it was found the following: 1) the characteristic scale of fluctuations that are responsible for the light scattering amounts to  $r \sim 10^{-5} \div 10^{-4}$  cm, and 2) the characteristic times of their dissipation amount to  $\tau_1 \approx 10^{-5}$  s and  $\tau_2 \approx 10^{-2}$  s.

Additional arguments in favor of the proposed approach to the problem of substance diffusion from the nucleus surface into the solution bulk can be obtained on the basis of dimensionality reasons. From this viewpoint, the self-diffusion coefficient [see Eq. (14)] should be constructed in terms of the energy of molecular thermal motion, the shear viscosity coefficient, the nucleus size, and the surface tension coefficient. The solution and nucleus densities can also play an insignificant role. The diffusion coefficient is proportional to the energy of molecular thermal motion, because the growth of the nucleus surface oscillation amplitude has to be observed, as the temperature increases ( $D \sim k_B T$ ). Concerning the viscosity coefficient, the irreversibility degree of surface oscillations, which also stimulates the growth of the diffusion coefficient, should also be proportional to the dynamic viscosity of the system or some of its powers ( $D \sim \eta$ ). The magnitude of diffusion coefficient should be larger for the lower surface tension ( $D \sim 1/\sigma$ ) or, more accurately, to the nucleus surface energy ( $D \sim 1/\sigma r_0^2$ ). Finally, for the dimensionality reasons, the nucleus density should be in the denominator. Ultimately,

$$D \sim \frac{k_B T \eta}{\sigma r_0^2 \rho},$$

where  $[D] = \frac{L^2}{T}$ .

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ФІЗИЧНА ПРИРОДА ЧАСУ  
РЕЛАКСАЦІЇ ВОДНО-СПИРТОВИХ РОЗЧИНІВ

## Резюме

Вивчено кінетику встановлення рівноваги водних розчинів спиртів. Запропоновано модель нерівноважного стану водно-спиртового розчину, згідно з якою повільну релаксацію розчину пов'язано з руйнуванням зародків нової фази. Процес руйнування описано за допомогою лагранжевого формалізму і теорії нуклеації. Зроблено розрахунки коефіцієнта самодифузії молекул з поверхні зародка, за допомогою якого проведено оцінку часу руйнування зародків і часу їх життя залежно від розміру. Встановлено зв'язок між коефіцієнтом дифузії у просторі зародків і коефіцієнтом молекулярної самодифузії з поверхні зародків. Проведено порівняння з наявними експериментальними даними.