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PROBLEM OF THE APPEARANCE OF ACOUSTIC WAVES IN DISSOLUTION OF SUBSTANCES

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In the present work, a theoretical model of the appearance of acoustic waves in dissolution of substances is suggested.

According to [1], the processes of crystallization and melting of a substance are accompanied by acoustic emission. Since upon melting and dissolution of a solid, passage of the latter to the liquid phase is observed, then by analogy it might be expected that the dissolution process will also be accompanied by acoustic emission. In [2, 3], the appearance of acoustic waves in dissolution of substances was revealed experimentally and regularities of the change in the parameters of the acoustic emission with the concentration of the solution and its temperature were established; however, in the literature, there is no information on the mechanism of the appearance of acoustic emission in dissolution of substances in a liquid.

In this paper, an attempt is made to simulate this phenomenon mathematically.

As is known, in dissolution of a solid substance in a liquid the volume of the solution is not equal to the sum of the volumes of the pure solvent and the solute, i.e., the partial molecular volumes of the solute differ from the partial volumes of the molecules in the solid state. This change in the volume equals [4]

$$\Delta V = nkT \frac{\partial \ln C_0}{\partial p} . \tag{1}$$

Formula (1) holds true only for weak solutions; the quantity ΔV can be both positive and negative depending on the sign of the derivative $\partial \ln C_0 / \partial p$. If with increase in the pressure the substance solubility grows, then $\Delta V < 0$.

At the current stage of the development of the theory there is no reliable evaluation of the change in the specific volume of the solute in the liquid; therefore one is forced to be guided only by experimental data. Thus, for example, at a temperature of 298.1 K the partial molecular volume of ammonia in water is 12.5% smaller than its usual molecular volume, whereas the volume of hydrogen fluoride in the same solvent is 50% greater than its usual volume [5].

In Table 1, borrowed from [5], we present the partial molecular volumes of the solute and the solvent in some aqueous solutions.

It is evident from the data of Table 1 that with increase in the concentration of the solute in the solvent, the partial molecular volumes V_1 of the latter decrease insignificantly and this decrease can be ignored. On the other hand, the partial molecular volumes of the solute change noticeably. This change for sugar can be represented in the form

$$V_2^* \cdot 10^{24} = V_2 \cdot 10^{24} \left(1 + \frac{8.7}{348.6} C \right),$$

and for ammonia, in the form

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TABLE 1. Partial Molecular Volumes of the Solute and the Solvent in Some Aqueous Solutions

Solution density, g/ml	Weight fraction of the solute, g/g	Concentration of the saturated solution, g/ml	Partial molecular volumes		Apparent molecular volume of the solute, $V_2^*\cdot 10^{24}$ ml
			solvent, $V_1^*\cdot 10^{24}$ ml	solute, $V_2^*\cdot 10^{24}$ ml	
Sugar at 298.1 K					
0.99709	0	0	29.803	348.54	348.54
1.03679	0.1	0.103679	29.795	350.09	349.40
1.07940	0.2	0.215880	29.780	351.80	350.28
1.12517	0.3	0.337551	29.749	353.69	351.34
1.17439	0.4	0.469756	29.698	355.44	352.49
1.22732	0.5	0.613660	29.611	357.41	353.67
Ammonia at 288 K					
0.980	0.0468	0.0459	29.73	39.74	40.32
0.960	0.080	0.941	29.75	39.63	40.01
0.940	0.1540	0.1447	29.79	39.21	39.72
0.920	0.2120	0.1950	29.88	38.74	39.60
0.900	0.2780	0.2501	30.12	38.12	39.31
0.980	0.3550	0.3123	30.63	37.27	38.87

$$V_2^* \cdot 10^{24} = V_2 \cdot 10^{24} \left(1 - \frac{5.5}{40.57} C\right).$$

We rewrite the last formulas in the following manner:

$$\Delta V / V = \Re C , \tag{2}$$

where $\Re = 2.4\cdot 10^{-2}$ for sugar and $\Re = -0.14$ for ammonia.

Thus, in dissolution of sugar in water the volume of the system increases, while in dissolution of ammonia, it decreases.

In the dissolution of a solid substance in a liquid the narrow zone in which detachment of molecules of the solid substance and their passage into solution occur, is a zone of disturbance of the liquid density.

The density change in this zone will extend over the entire volume of the liquid in the form of acoustic signals; in other words, from the zone of dissolution of the substance, emission of acoustic waves will occur.

As a model of propagation of acoustic waves from the zone of dissolution of substances in a liquid, we consider a cylindrical vessel filled with a solvent at the bottom of which a solid substance with a thickness identical in all directions is located. The scheme of the dissolution of the substance is given in Fig. 1.

Suppose that h_0 is the initial thickness of the layer of the solid and h is the height of the liquid layer. When $t = 0$, a barrier between the liquid and the solid is removed and from this instant of time the process of dissolution of the solid substance in the liquid begins. Now we formulate the corresponding mathematical problem.

The concentration of the solution is described by the diffusion equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} , \quad \xi < x < h , \tag{3}$$

where D is the diffusion coefficient of molecules of the solid substance in the solvent.

The solution of Eq. (3) must satisfy the following conditions:

$$C(\xi, t) = C_0 , \tag{4}$$

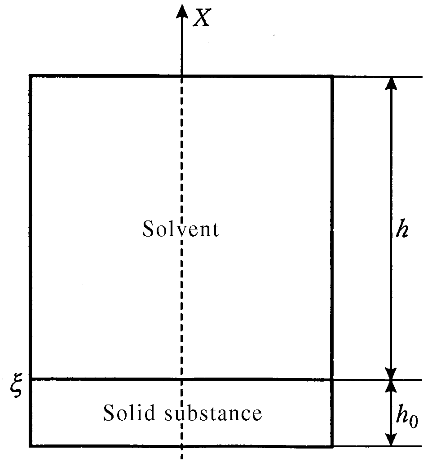

Fig. 1. Scheme of dissolution of a substance

$$\left.\frac{\partial C}{\partial x}\right|_{x=h} = 0\,, \tag{5}$$

i.e., the upper boundary is impenetrable to molecules of the dissolving substance.

The lower boundary of the integration domain of Eq. (1) is mobile; here, the law of motion of this limit is not given in advance, and it must be found in the process of solving the problem. Thus, we have a typical Stefan problem.

In the experiments, the thickness h of the solution layer is about 0.1–0.2 m. The time needed for establishment of the equilibrium concentration (the relaxation time) τ in the solution is equal to h^2/D. Usually, the coefficient $D \sim 10^{-9}$ m^2/sec, and then $\tau \sim 10^7$ sec.

These evaluations show that, in the time of the experiment (of the order of an hour), virtually no molecules of the dissolving substance reach the solution surface; in other words, it can be assumed that $h \sim \infty$ and instead of the condition $\xi < x < h$ we obtain $\xi < x < \infty$, while at infinity $C = C_\infty$, C_∞ is the initial concentration of the solvent. (Frequently, the solvent contains impurities, for example, a small amount of table salt is present in drinking water; therefore we will consider the case where $C_\infty \neq 0$).

Thus, instead of condition (5) we give

$$C\,|_{x=\infty} = C_\infty\,. \tag{6}$$

The initial conditions have the form

$$C\,(x, 0) = C_\infty\,, \quad \xi < x < \infty\,. \tag{7}$$

Problem (3)-(7) is already self-similar, i.e., in its conditions the length does not appear. We write the solution of Eq. (3) in the following manner:

$$C = C_\infty + \frac{C_0 - C_\infty}{\Phi^*\,(\alpha)}\,\Phi^*\left(\frac{X}{2\sqrt{Dt}}\right), \quad \xi < x < \infty\,, \tag{8}$$

where $\Phi^* = 1 - \Phi(x)$. Here the law of motion of the solution–solid interface has the form

$$\xi = 2\alpha\sqrt{Dt}\,, \tag{9}$$

where α is determined from the equation

$$\frac{C_0 - C_\infty}{\Phi^* (\alpha)} \exp(-\alpha^2) = 2\alpha C_0 \, . \tag{10}$$

Equation (10) is transcendental. The coefficient α is usually small; therefore, in a first approximation, from Eq. (10) we obtain

$$\alpha = \frac{1}{2}\left(1 - \frac{C_\infty}{C_0}\right). \tag{11}$$

In 1 sec, the solid–solution interface moves a distance equal to ξ; here, the relative volume of the system changes by a quantity β determined from formula (2), $\beta = \Re \, (C_0 - C_\infty)$.

Thus, it can be considered that the lower boundary of the liquid moves according to the law

$$u\,|_{x=\xi} = \beta \, \xi \, (t) \, . \tag{12}$$

As a result of the motion of the lower boundary of the liquid, the latter will execute vibrational motion, i.e., in the liquid a system of standing waves with different frequencies that are multiples of the fundamental frequency $\nu = a/2h$ is established. To find the parameters of these waves, we must solve the wave equation

$$\frac{\partial^2 u}{\partial t^2} = a^2 \frac{\partial^2 u}{\partial x^2} \, , \quad \xi < x < h \, , \tag{13}$$

which should satisfy the conditions

$$u\,(x, 0) = 0 \, , \quad u_t\,(x, 0) = 0 \, ; \tag{14}$$

$$u\,(\xi, t) = \beta \, \xi \, (t) \, . \tag{15}$$

Let us assume that the solvent surface is open. Then we will have

$$\left.\frac{\partial u}{\partial x}\right|_{x=h} = 0 \, . \tag{16}$$

Boundary condition (15) is inhomogeneous. In order that the method of separation of variables can be applied to problem (13)-(16), we reduce it to a problem with homogeneous boundary conditions. For this purpose, we will seek the function $u(x, t)$ in the form of the sum

$$u\,(x, t) = \beta \, \xi \, (t) + \vartheta \, (x, t) \, , \tag{17}$$

where $\vartheta(x, t)$ is the solution of the following problem:

$$\begin{gathered} \frac{\partial^2 \vartheta}{\partial t^2} = \alpha^2 \frac{\partial^2 \vartheta}{\partial x^2} - \beta \ddot{\xi} \, , \quad \vartheta\,(x, 0) = 0 \, , \quad \vartheta_t\,(x, 0) = -\beta \dot{\xi} \, , \\ \vartheta\,(\xi, t) = 0 \, ; \quad \left.\frac{\partial \vartheta}{\partial x}\right|_{x=h} = 0 \, . \end{gathered} \tag{18}$$

The functions $X(x) = \sin \lambda_n x - \tan \lambda_n \xi \, \cos \lambda_n x$, where $\lambda_n = \pi(2n + 1)/(n - \xi)2$, are eigenfunctions of problem (18). The square of the norm of the eigenfunctions is equal to

$$\|X_n^2\| = \frac{h - \xi}{2} (1 + \tan^2 \lambda_n h) .$$

The solution of problem (18) can be represented in the form

$$\vartheta (x, t) = - \beta \sum_{n=0}^{\infty} \frac{\cos \lambda_n (h - \xi)}{\lambda_n \|X_n^2\|} \left[\int_0^t \dot{\xi} (\tau) \cos \omega_n (t - \tau) \, d\tau \right] X_n (x) , \tag{19}$$

where

$$\omega_n = a\lambda_n = \frac{\pi a (2n + 1)}{2 (h - \xi)} .$$

Substituting the value of $\dot{\xi}(t)$ from Eq. (9) into Eq. (19), we obtain

$$\vartheta (x, t) = - \frac{\beta (C_0 - C_\infty)}{2C_0} \sqrt{D} \sum_{n=0}^{\infty} \frac{\cos \lambda_n (h - \xi)}{\lambda_n \|X_n^2\|} \times$$

$$\times \left[\int_0^t \frac{1}{\sqrt{\tau}} \cos \omega_n (t - \tau) \, d\tau \right] X_n (x) . \tag{20}$$

It can be shown that on the right-hand side of Eq. (20) the integral is

$$J = \int_0^t \frac{\cos \omega_n (t - \tau) \, d\tau}{\sqrt{\tau}} = \frac{\sqrt{2\pi}}{\sqrt{\omega_n}} [C (\omega_n t) \cos \omega_n t + S (\omega_n t) \sin \omega_n t] . \tag{21}$$

As is known [6], for $z = \omega_n t >> 1$ the following asymptotic formulas hold:

$$S (z) = \frac{1}{2} - \frac{\cos z}{\sqrt{2\pi z}} , \quad C (z) = \frac{1}{2} + \frac{\sin z}{\sqrt{2\pi z}} . \tag{22}$$

Substitution of Eq. (22) into Eq. (21) yields

$$J \approx \frac{\sqrt{\pi}}{\sqrt{2\omega_n}} [\cos \omega_n t + \sin (\omega_n t)] .$$

Thus, for $\vartheta(x, t)$ we will have

$$\vartheta (x, t) = - \frac{\beta (C_0 - C_\infty) \sqrt{D\pi}}{2 \sqrt{2} \, C_0} \sum_{0}^{\infty} \frac{\cos \lambda_n (h - \xi)}{\lambda_n \|X_n^2\| \sqrt{\omega_n}} (\cos \omega_n t + \sin \omega_n t) X_n (x) .$$

Finally, for $u(x, y)$ we write

$$u (x, t) = \beta \, \xi (t) - \frac{\beta (C_0 - C_\infty)}{2C_0} \sqrt{\left(\frac{\pi D}{2} \right)} \sum_{n=0}^{\infty} \frac{\cos \lambda_n (h - \xi)}{\lambda_n \|X_n^2\| \sqrt{\omega_n}} \times$$

$$\times (\cos \omega_n t + \sin \omega_n t) X_n (x) . \tag{23}$$

The first term of equality (23) gives the displacement of the interface of solution–solid substance, and the second, the vibrational motion of the solution.

Usually, in experiments $\xi << h$; therefore, in Eq. (23) the quantity ξ can be ignored compared to h. Then we obtain

$$u\,(x,\,t) = \beta\,\xi\,(t) + \frac{2\beta\,(C_0 - C_\infty)}{\pi C_0}\sqrt{\left(\frac{Dh}{a}\right)}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^{3/2}}\times$$

$$\times\,(\cos\omega_n t + \sin\omega_n t)\,\sin\frac{\pi\,(2n+1)x}{2h}\,.$$

The additional dynamic pressure can be found from the equality

$$p\,(x,\,t) = -\frac{1}{K}\frac{\partial u}{\partial x}\,.$$

Hence we will have

$$p\,(x,\,t) = \frac{\beta\,(C_0 - C_\infty)}{KC_0}\sqrt{\left(\frac{D}{2ah}\right)}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^{1/2}}\sin\left(\omega_n t + \frac{\pi}{4}\right)\times$$

$$\times\cos\frac{\pi\,(2n+1)\,x}{2h}\,. \tag{24}$$

The fundamental frequency is $\omega_1 = \pi a/2h$; for water, a = 1500 m/sec, and the characteristic value of h is equal to 0.1 m. Then we obtain $\omega_1 = 2{\cdot}10^4$ sec^{-1}, i.e., the fundamental frequency is $\nu_1 \sim 10^4$ sec^{-1}.

From Eq. (24) it follows that the maximum amplitude of the pressure in the acoustic wave is equal to

$$p_{\max} \approx \frac{\beta\,(C_0 - C_\infty)}{KC_0}\sqrt{\left(\frac{D}{2ah}\right)}.$$

For sugar, $\beta = 10^{-2}$ and $D \sim 10^{-9}$ m^2/sec; for water, $1/K = 10^9$ Pa. Then for h = 0.1 m we obtain $p \sim 10^2$ Pa, which is in good agreement with experimental data of [2, 3].

However, the value of the frequency ω is 1-2 orders of magnitude smaller than the experimental data for this frequency. The picture of the behavior of the function $p(x,\ t)$ in the experiments leads us to the idea of the existence of resonance phenomena in dissolution of solid substances in a liquid. Therefore, the above model of the appearance of acoustic emission in dissolution of substances needs some correction, for which purpose, apparently, it is necessary to also take into account the vibrational motion of the solid substance.

NOTATION

n, number of atoms of the solute per unit volume; $C_0 = n/N$, concentration of the saturated solution; N, number of solvent molecules per unit volume; C, concentration; β, coefficient of volumetric expansion of the substance; $\Re$, coefficient of volumetric expansion of individual molecules in passage from the solution to the solid phase; ξ, coordinate of the solid–liquid interface; τ, delay time; $\Phi(x)$, error integral; ν, frequency of vibrations of the standing waves; a, speed of sound in the solvent; $S(z)$ and $C(z)$, Fresnel integrals; $u(x,\ t)$, longitudinal displacement of a liquid particle in the acoustic wave; T, absolute temperature; K, coefficient of liquid compressibility; $p(x,\ t)$, dynamic pressure; points above a symbol denote differentiation with respect to time.

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