Investigation of self-diffusion of molecules of liquid in media with random obstacles by the stimulated-spin-echo method

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A nuclear spin-echo method makes it possible to measure the mean value of the temporal autocorrelation function, $\langle \mathbf{f}(t)\mathbf{f}(0)\rangle$, where $\mathbf{f}(t)$ is the force of the interaction between a liquid molecule and the surface of a porous system at the time t. Quartz sand was used as the porous material, and normal tridecane as the low-molecular liquid, in the experiments. The dependence of the correlation function $\langle \mathbf{f}(t)\mathbf{f}(0)\rangle$ on the time, the radius of the sand grains, and the concentration of the liquid was studied. The experimental results agree satisfactorily with previous theoretical predictions by N. F. Fatkullin [JETP **71**, 1141 (1990)].

1. INTRODUCTION

Diffusion of molecules in random fields is a classical problem in the physics of disordered media and has been studied for many decades (see, for example, the reviews Refs. 1 and 2). Nontrivial examples of disordered media are porous systems or, which is the same thing, systems with random obstacles.

Self-diffusion of molecules of a low-molecular liquid in porous media has been studied time and again, both theoretically and experimentally (see, for example, Refs. 3–10). These works were primarily concerned with analysis of the dependence of the self-diffusion coefficients of the molecules of liquid on the concentration of obstacles in the system.

Diffusive damping of the amplitude of the spin echo of a particle moving in a random field was studied theoretically in Ref. 11. It follows from the results of this work that one of the main objects of experimental investigations should be the time dependence of the average (also sometimes called effective) self-diffusion coefficient $D^*(t_D)$ for short diffusion times t_D. It was found that the derivative $dD^*(t_D)/dt_D$ is more informative than the limiting value $d^* = \lim_{t_D\to\infty} D^*(t_D)$, which is essentially what the authors of all preceding works known to us studied (see Refs. 3–10).

In the present paper we present the results of an experimental investigation specially designed for studying the time dependence of the effective self-diffusion coefficient $D^*(t_D)$, which contains new information about the autocorrelation function of the force of interaction of a molecule with the surface of a porous system. We also develop a number of theoretical assumptions made in Ref. 11.

2. CHARACTERISTICS OF THE OBJECTS AND METHOD OF INVESTIGATION

The objects of investigation were chemically pure tridecane (TD) as the model liquid and fractions of quartz sand with particle radii $r_0 = 0.04$–0.05, 0.10–0.12, and 0.15–0.18 mm as the porous media. These materials are easily accessible and are important in practice (for example, for development of oil fields). The volume fractions of tridecane in the specimen studied ranged from 0.06 to 0.26. The sand fractions were first washed in distilled water and dried at 100 °C for 8 hours, after which the tridecane was introduced.

The specimens were sealed in test tubes of 7 mm diameter and allowed to stand for several hours at 80 °C in order to establish in them thermodynamic-equilibrium states. The porosities, i.e., the ratios of the pore volume to the total volume of the system, fall into the range 0.33–0.45 for the sands investigated in the present work.[12] The volume fractions of liquid did not exceed 0.26. Hence it is obvious that liquid did not occupy the entire pore space. It can apparently be assumed that liquid is present in the specimens in the form of a layer with thickness h around each sand grain; microscopic investigations confirm this picture.

Assuming that each sand grain is a sphere of radius r_0 and neglecting the mutual touching of the grains, the quantity h can be estimated from the following relation:

$$h = \frac{1}{3}\frac{\rho_2}{\rho_1}\frac{\omega_1}{1-\omega_1} r_0, \qquad (1)$$

where ρ_1 and ρ_2 are the density of tridecane and sand, respectively, and ω_1 is the mass fraction of tridecane.

Table I gives the designations and the characteristics of the specimens studied as wells the values of h.

The self-diffusion parameters were measured by the method of NMR (stimulated echo) on protons with a pulsed gradient magnetic field. The maximum value of the magnetic field gradient was 50 T/m and the resonance frequency was 60 MHz. The laboratory diffusometer is described in Refs. 13 and 14. The diffusion times t_D ranged from 3 to 310 ms; the measurements were performed at 30 °C.

The experimental errors of measurement of $A(g^2)$, of the coefficient of self-diffusion, and of the parameter σ did not exceed 10% under the most unfavorable conditions.

3. EXPERIMENTAL RESULTS

In low-molecular liquids the measured amplitude of the diffusive damping of the spin-echo signal is described by the very simple expression (see, for example, Refs. 5, 13, and 14 and the extensive literature cited there):

$$A(g^2) = A(0)\exp(-\gamma^2\delta^2 g^2 D_0 t_D), \qquad (2)$$

where g and δ are the magnitude and duration of the pulsed gradient magnetic field, $A(0)$ is the intensity of the ampli-

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TABLE I. Designations, characteristics of the investigated specimens, and some parameters describing the process of self-diffusion in tridecane-sand systems.

Specimen No.	Tridecane content in the specimen, vol. %	$r_0 \cdot 10^2$, mm	σ^2	h^2, mm^2	$D_0 t_D$, mm^2	τ_f/τ_0	$\langle \mathbf{f}(t)\mathbf{f}(0)\rangle$ $*\mathrm{H}^2$ (t_D = 3 ms)
1	6	4–5	1,21	10^{-6}	$5\cdot10^{-6}$	–	–
2	12	4–5	0,39	$6\cdot10^{-6}$	$5\cdot10^{-6}$	–	–
3	17	4–5	0,28	10^{-5}	$5\cdot10^{-6}$	0,11	$5\cdot10^{-30}$
4	26	4–5	0,02	$3\cdot10^{-5}$	$5\cdot10^{-6}$	–	–
4	26	4–5	0,14	$3\cdot10^{-5}$	$5\cdot10^{-5}$	0,14	$4\cdot10^{-30}$
4	26	4–5	0,19	$3\cdot10^{-5}$	$2\cdot10^{-4}$	–	–
5	26	10–12	–	–	–	0,17	$1,8\cdot10^{-30}$
6	23	15–18	0	10^{-3}	10^{-5}	0,20	$1,3\cdot10^{-30}$
6	23	15–18	0	10^{-3}	$2\cdot10^{-4}$		

tude of the spin-echo with $g = 0$, D_0 is the self-diffusion coefficient of the pure liquid, and γ is the proton gyromagnetic ratio.

In our specimens (the numbers of the specimens are given in Table I) the form of the diffusive damping was more complicated (see curves *1–6* in Fig. 1). The equation (2) described diffusive damping only in specimen No. 6 (curves *7* and *8* in Fig. 1) which had the largest sand grains ($r_0 = 0.18$ mm).

The diffusive damping of the other specimens (Nos. 1–5) was described in the standard manner (see Refs. 13 and 14):

$$A(g^2)=A(0)\int_0^{\infty}\exp(-\gamma^2\delta^2 g^2 D t_D)P(D)\,dD, \tag{3}$$

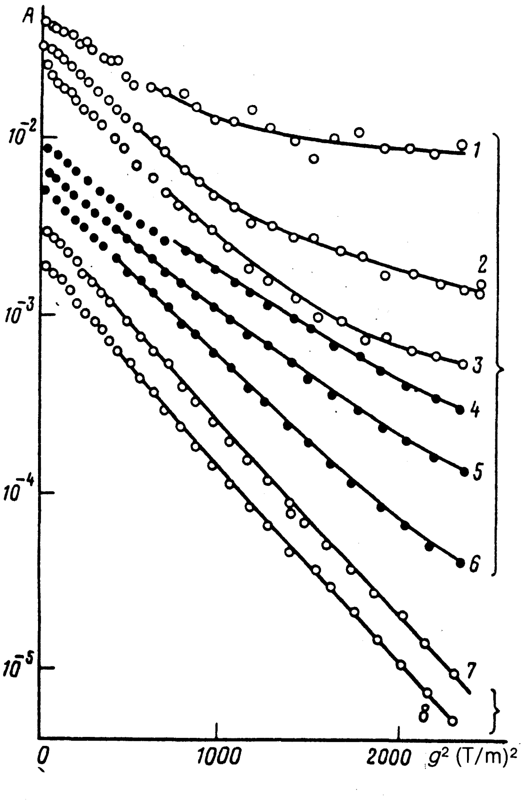

FIG. 1. Diffusive-damping curves for specimens Nos. 1 (curves *1*), No. 2 (*2*), and No. 3 (*3*) with $t_D = 6$ ms; specimen No. 4 with $t_D = 310$ ms (*4*), 62 ms (*5*), and 6 ms (*6*) and specimen No. 6 with $t_D = 310$ ms (*7*) and 13 ms (*8*). The measurement temperature was equal to 30 °C.

where $P(D)$ is the distribution of effective self-diffusion coefficients, assumed to be the log-normal distribution

$$P(D)=\frac{1}{(2\pi\sigma^2)^{1/2}}\exp\left[-\frac{\ln^2(D/D_n)}{2\sigma^2}\right]. \tag{4}$$

The parameters D_n and σ^2 of the distribution (4) were chosen by fitting the expression (3) to the measured values of $A(g^2)$. The parameter D_n is the most probable value of the effective self-diffusion coefficient and the parameter σ^2 describes the width of the apparent distribution of the self-diffusion coefficients. The values of these parameters are presented in Table I for different diffusion times t_D.

It is obvious from Fig. 1 and the data on σ^2 that the form of the diffusive-damping curve for specimens Nos. 1–5 depends on the diffusion time and on the amount of liquid in the specimen:

1) As the diffusion time t_D increases the diffusive-damping curve tends to deviate from the exponential behavior (3) (see curves *4–6* in Fig. 1).

2) For constant t_D the quantity σ^2 increases with decreasing tridecane content (curves *1–3* and *6*).

In such cases a reliably measured characteristic of the motion is the average self-diffusion coefficient $D^*(t_D)$, which is determined from the initial slope of the function $\ln A(g^2)$ (see Refs. 11, 13, and 14). The average self-diffusion coefficient D^* is presented in Fig. 2 as a function of the time t_D. It is obvious that for $t_D \leqslant 40$–60 ms D^* depends strongly on the diffusion time, and for $t_D \geqslant 100$ ms this de-

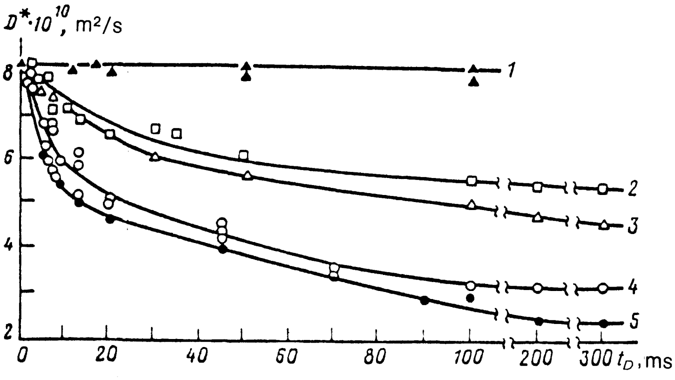

FIG. 2. Average self-diffusion coefficient D^* as a function of the diffusion time t_D for pure tridecane (curves *1*), specimen No. 6 (*2*), No. 5 (*3*), No. 4 (*4*), and No. 3 (*5*).

pendence virtually vanishes. The form and position of the curves $D^*(t_D)$ and the value of D^* depend on the concentration of the liquid in the specimen and the size of the sand grains. Obviously, the self-diffusion coefficient of pure tridecane does not depend on the diffusion time t_D.

4. SOME THEORETICAL ASPECTS OF THE PROBLEM

To make the presentation more coherent we deemed it possible to begin this section, right up to the formula (9) inclusive, by examining the results of our Ref. 11, where we investigated the general properties of self-diffusion and diffusive damping of the spin-echo signal of a particle in a nonuniform medium. The effect of the nonuniformities of the medium on the particle motion was described in terms of an effective potential $U(\mathbf{r})$. It was assumed that the Green's function $W(\mathbf{r},t)$ of the particle, i.e., the probability distribution of displacement of a particle by the radius vector $\mathbf{r}$ in a time t, satisfies the Smoluchowski equation

$$\frac{\partial}{\partial t} W(\mathbf{r},t)=D_0\frac{\partial}{\partial \mathbf{r}}\left(\frac{\partial}{\partial \mathbf{r}}-\frac{\mathbf{f}(\mathbf{r})}{k_BT}\right)W(\mathbf{r},t), \tag{5}$$

where D_0 is the self-diffusion coefficient of a particle in a pure liquid, $\mathbf{f}(\mathbf{r}) = -\partial U(\mathbf{r})/\partial \mathbf{r}$ is the random force exerted by the nonuniformities of the system on a particle located at the point $\mathbf{r}$, k_B is Boltzmann's constant, and T is the temperature.

The diffusive-damping amplitude, which is the van Hove incoherent dynamic structure factor, satisfies the equation

$$\frac{d}{dt}A(k^2,t)=-k^2D_0A(k^2,t)+i\frac{D_0}{k_BT}\mathbf{k}\int W(\mathbf{r},t)e^{-i\mathbf{k}\mathbf{r}}\mathbf{f}(\mathbf{r})d^3r. \tag{6}$$

were $\mathbf{k}=\gamma\delta\mathbf{g}$ is the "wave vector" describing the spatial nonuniformity induced in the magnetic field in the system by the gradient of the magnetic field.

The solution of Eq. (6) up to terms of order k^6 can be written in the following form:

$$A(k^2,t_D)=\exp[-k^2\alpha_1(t_D)+k^4\alpha_2(t_D)+\ldots]. \tag{7}$$

where $\alpha_1(t_D)=D^*(t_D)\cdot t_D$ is one-sixth the rms displacement of molecules in a time t_D, $D^*(t_D)$ is the effective self-diffusion coefficient of a molecule in a diffusion time t_D, and $\alpha_2(t_D)$ is a positive-definite function describing the initial nonexponential nature of the amplitude of diffusive damping.

The following limiting cases exist (see Ref. 11):

$$\alpha_2(t_D)\approx 0,\quad \text{if}\quad \xi^2\gg D_0t_D, \tag{8a}$$

$$\alpha_2(t_D)t_D^{-2}\approx 0,\quad \text{if}\quad \xi^2\ll D_0t_D, \tag{8b}$$

where ξ is the correlation radius of the random field $\mathbf{f}(\mathbf{r})$.

In stimulated-spin-echo experiments $\delta^2t_D = \text{const}$. For this reason, as can be seen from the relations (7) and (8a,b), the diffusive damping of the spin echo deviates strongly from exponential behavior only at times of the order of $D_0t_D\approx\xi^2$, i.e., as t_D increases the nonexponential behavior of the amplitude $A(k^2,t_D)$ passes through a maximum and is small for long and short times.

The initial rate of change of the average self-diffusion coefficient $D^*(t_D)$ satisfies the equation

$$\frac{d}{dt_D}D^*(t_D)\big|_{t_D=0}=-\frac{1}{6}\left(\frac{D_0}{k_BT}\right)^2\langle\mathbf{f}^2(\mathbf{r})\rangle_{eq}, \tag{9}$$

where $\langle\mathbf{f}^2(\mathbf{r})\rangle_{\text{eq}}$ is the mean-square force exerted at equilibrium on the particle by the nonuniformities of the system.

This formula indicates that it is in principle possible to measure the variance of the random field $\mathbf{f}(\mathbf{r})$. In practice, however, the extrapolation to zero $t_D\to 0$ cannot always be done reliably, since the apparatus has a "dead" time τ_{ap}, below which t_D cannot be reduced.

If $\tau_{\text{ap}}\gg a_0^2/D_0$, where a_0 is the characteristic range of the random force $\mathbf{f}(\mathbf{r})$, which happens for the systems discussed in the present paper, then when the measured derivative $dD^*(t_D)/dt_D$ is extrapolated to $t_D=0$ one actually obtains not the true value (9) but rather some value of the derivative in the time interval $0<t_D<\tau_{\text{ap}}$. It is thus necessary to find for the relation (9) an analog that takes into account the circumstances mentioned above.

In Ref. 11 it was shown that the average self-diffusion coefficient $D^*(t_D)$ is connected with the instantaneous self-diffusion coefficient $\tilde{D}(t_D)$ by the relation

$$D^*(t_D)=\frac{1}{t_D}\int_0^{t_D}d\tau\tilde{D}(\tau). \tag{10}$$

The instantaneous self-diffusion coefficient satisfies in turn the equation

$$\frac{d}{dt}\tilde{D}(t)=-\frac{1}{3}\left(\frac{D_0}{k_BT}\right)^2\langle\mathbf{f}(t)\mathbf{f}(0)\rangle, \tag{11}$$

where $\mathbf{f}(0)$ is the random force acting on the particle initially, $\mathbf{f}(t)$ is the value of this force at the time t, and the brackets denote averaging over all random trajectories of the particle.

To avoid misunderstandings, we note that the time dependence of the random force $\mathbf{f}(t)$ is caused by the displacements of the particles in space, i.e.,

$$\mathbf{f}(t)\equiv\mathbf{f}(\mathbf{r}(t)).$$

The following expression can be easily derived with the help of the relations (10) and (11):

$$\frac{D_0-D^*(t_D)}{t_D}=\frac{1}{3}\left(\frac{D_0}{k_BT}\right)^2\frac{1}{t_D^2}\int_0^{t_D}dt_1\int_0^{t_1}dt_2\langle\mathbf{f}(t_2)\mathbf{f}(0)\rangle. \tag{12}$$

Hence one can see that the average derivative of the average self-diffusion coefficient $D^*(t_D)$ at a finite moment in time contains information about the time-averaged correlation function defined by the relation

$$\langle\mathbf{f}(t_D)\mathbf{f}(0)\rangle^*\equiv\frac{1}{t_D^2}\int_0^{t_D}dt_1\int_0^{t_1}dt_2\langle\mathbf{f}(t_2)\mathbf{f}(0)\rangle. \tag{13}$$

In accordance with this definition, we rewrite the relation (12) in the following form:

$$\frac{D_0-D^*(t_D)}{t_D}=\frac{1}{3}\left(\frac{D_0}{k_BT}\right)^2\langle\mathbf{f}(t_D)\mathbf{f}(0)\rangle^*. \tag{14}$$

We also note that for short times $t_D\ll a^2/D_0$ the relations (14) and (12) transform into the relation (9). This can be verified by expanding the correlation function

$\langle \mathbf{f}(t)\mathbf{f}(0)\rangle$, contained on the right-hand side of Eq. (12), in a Taylor series.

The exact calculation of the correlation function $\langle \mathbf{f}(t)\mathbf{f}(0)\rangle^*$ is a nontrivial mathematical problem, whose solution we do not know. Reasonable estimates can be obtained, however, in the case when the obstacles are a system of randomly distributed spheres with radius r_0 and volume concentration φ, and the interaction with the molecules is repulsive and described by the potential

$$U(\mathbf{r})=\begin{cases}\varepsilon/|r-r_0|^n, & r\geqslant r_0,\\ \infty, & r\leqslant r_0\end{cases} \tag{15}$$

where ε is the energy parameter and r is the distance between the molecule and the center of a given sphere.

We note first that the correlation function of interest can be calculated exactly for $t_D=0$:[11]

$$\langle \mathbf{f}(0)\mathbf{f}(0)\rangle^*=\frac{1}{2}\langle \mathbf{f}^2(\mathbf{r})\rangle_{eq}=\frac{3n}{2}\Gamma\left(2+\frac{1}{n}\right)\frac{(k_BT)^2}{r_0a_0}\frac{\varphi}{1-\varphi}. \tag{16}$$

where $\Gamma(x)$ is the gamma function and $a_0=(\varepsilon/k_BT)^{1/n}$ is the effective range of the repulsive forces and in our case can be considered to be the depth of the surface layer; we assumed that $a_0\ll r_0$.

We shall interpret the structure of the formula (16) with the help of a relation which makes the result itself obvious:

$$\langle \mathbf{f}^2(\mathbf{r})\rangle_{eq}\approx\left(\frac{k_BT}{a_0}\right)^2\left(\frac{r_0{}^2a_0}{r_0{}^3}\frac{\varphi}{1-\varphi}\right), \tag{17}$$

where k_BT/a_0 is of the order of the repulsive forces acting on a molecule in the surface layer, $r_0^2a_0$ is of the order of the volume of the effective interaction of the molecule with a separate obstacle, and $r_0^3(1-\varphi)/\varphi$ is of the order of the free volume per separate obstacle.

From this interpretation it is clear that the factor

$$\frac{r_0{}^2a_0}{r_0{}^3}\frac{\varphi}{1-\varphi}$$

is proportional to the probability of finding a molecule at a distance of the order of a_0 from some obstacle.

We now estimate the correlation function $\langle \mathbf{f}(t)\mathbf{f}(0)\rangle^*$. We start from the fact that a molecule of the liquid interacts effectively with an obstacle only at distances of the order of a_0; this is formally reflected by the representation (17). For this reason, when calculating the correlation function $\langle \mathbf{f}(t)\mathbf{f}(0)\rangle^*$ from the formula (13) only the times when the molecule is located in the surface layer will contribute to the time integral.

Hence it is obvious that the correlation function of interest to us can be estimated as

$$\langle \mathbf{f}(t)\mathbf{f}(0)\rangle^*\approx\langle \mathbf{f}^2(\mathbf{r})\rangle_{eq}\frac{t_1}{t_D}, \tag{18}$$

where t_1 is the total residence time on the surface of a given obstacle, taking into account all returns within the time t_D, under the condition that initially the molecule is located in the surface layer.

We consider the spatial displacements of the molecules to be a series of random jumps, each of length l. We designate by τ_0 the so-called "settled" lifetime or, equivalently, the time of a "jump" of a molecule in the pure liquid. We take into account the interaction of a molecule with the surface of the obstacles by means of the parameter τ_1—the "settled" lifetime of a molecule on the surface of the obstacles. It is obvious that the time τ_1 is a function of the interaction potential $U(\mathbf{r})$.

Let N_0 be the total number of jumps a molecule makes outside the surface layer and let N_1 be the number of jumps occurring over the same time interval within the surface layer. We now write the obvious relation

$$N_0\tau_0+N_1\tau_1=t_D. \tag{19}$$

Let the diffusion time be quite long, i.e., $D_0t_D\gg a_0^2$. In such cases, for any reasonable ratios of τ_0 and τ_1, we have $N_0\gg N_1$ and the second term in the formula (19) $t_1=\tau_1N_1$ can be neglected:

$$N_0\tau_0\approx t_D. \tag{20}$$

We impose one other constraint on the diffusion time:

$$D_0t_D\ll r_0{}^2, \tag{21}$$

i.e., we study times when the motion of the molecule is concentrated in a neighborhood of some one sphere.

All contacts between the molecule under study, with the exception of the first one, and the surface of an obstacle are repeated returns. For this reason, the last contact occurs at a distance of the order of $lN_0^{1/2}$ from the first one. Hence it is understandable that the volume of the surface layer in which all contacts with the surface are concentrated is of the order of

$$V_{sl}\approx a_0(lN_0{}^{1/2})^2=a_0l^2N_0.$$

The trajectory of a molecule is distributed in a volume of the order of

$$V\approx(lN_0{}^{1/2})^3=l^3N_0{}^{3/2}.$$

Assuming that the trajectory of a molecule is distributed randomly over the entire volume V (this is intuitively reasonable), we estimate the number of hops of a molecule in the surface layer as follows:

$$N_1\approx N_0\frac{V_{sl}}{V}\approx N_0{}^{1/2}\frac{a_0}{l}. \tag{22}$$

Using now the relation $D_0\simeq l^2/\tau_0$ and $t_1=\tau_1N_1$ as well as the formula (16), we transform the relation (18) into the form

$$\langle \mathbf{f}(t)\mathbf{f}(0)\rangle^*\approx\langle \mathbf{f}^2(\mathbf{r})_{\text{eq}}\frac{a_0}{(D_0t_D)^{1/2}}\frac{\tau_1}{\tau_0}$$

$$=3n\Gamma\left(2+\frac{1}{n}\right)\frac{(k_BT)^2}{r_0(D_0t_D)^{1/2}}\frac{\tau_1}{\tau_0}\frac{\varphi}{1-\varphi}. \tag{23}$$

5. DISCUSSION

We begin by analyzing the *form of diffusive damping* as a function of the tridecane content and the diffusion time t_D. It follows from the relation (7) that in the general case the amplitude of diffusive damping $A(g^2)$ is nonexponential. Its behavior becomes simpler only if the conditions (8a) and (8b), which contain the correlation radius ξ of the random field, are satisfied. Our systems have two characteristic lengths: the average thickness h of the liquid on the surface of the sand grains and the average radius r_0 of the sand grains.

It is obvious from the data in Table I that $h < r_0$ in all cases which we investigated. It is obvious that in our systems the thickness of the layer of liquid should play the role of the parameter ξ in the relation (8a), while in the relation (8b) the quantity r_0 will play the role of this parameter.

The values of the quantities $D_0 t_D$, for which the form of diffusive damping of the spin-echo signal was investigated, are presented for different specimens in the sixth column of Table I. It is obvious that for specimen No. 6, for example, with $t_D = 13$ ms, the condition (8a) is satisfied very accurately; for $t_D = 310$ ms, however, the same condition is not satisfied as well, but it is still satisfied. Hence it follows that in these cases $\alpha_2 \approx 0$ and the diffusive damping should be exponential; this has, in fact, been observed experimentally (curves *7* and *8* in Fig. 1).

For specimen No. 4 with $t_D = 6$ ms (curve *6*, Fig. 1) $h^2 > D_0 t_D$. These values are, however, almost comparable. It is clear that the diffusive damping is slightly nonexponential. As the content of liquid in the system decreases (specimens Nos. 3, 2, and 1) the nonexponential behavior of their diffusive damping becomes increasingly stronger. The ratio of the characteristic parameters in this case varies as $D_0 t_D \lesssim h^2$, $D_0 t_D \approx h^2$ and $D_0 t_D \gtrsim h^2$, but in all of these cases the condition (8b), i.e., $r_0^2 \ll D_0 t_D$, does not hold. This is why the nonexponential behavior intensifies.

The small change in diffusive damping accompanying a change in t_D can be explained analogously (curves *4–6* in Fig. 1). For technical reasons, however, the conditions (8b), unfortunately, could not be satisfied experimentally.

Thus the proposed theory explains satisfactorily the observed tendency for the form of the diffusive damping in the specimens studied to change with the sizes of the sand grains, the amount of liquid, and the diffusion time.

The observed dependence of the average self-diffusion coefficient $D^*(t_D)$ on the time t_D (Fig. 2) makes it possible to obtain with the help of the relation (14) information about the correlation function $\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^*$. The time dependence of the quantities $(D_0 - D^*(t_D))/t_D$, which is proportional to the correlation function $\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^*$, is presented in Fig. 3. It is obvious from this figure that

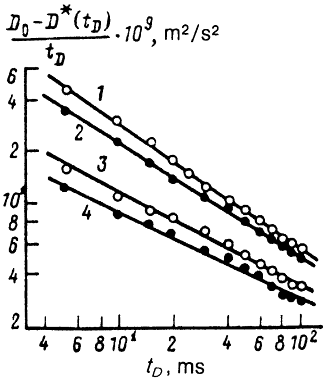

FIG. 3. Parameter $(D_0 - D^*(t_D))/t_D$ as a function of the diffusion time t_D for specimens No. 3 (curve *1*), No. 4 (*2*), No. 5 (*3*), and No. 6 (*4*). The measurement temperature is equal to 30 °C.

$$\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^* \propto t_D^{-n}. \tag{24}$$

where $n = 0.5$–0.7. In addition, for specimens with larger obstacles (specimens Nos. 5 and 6), for which the dependence $D^*(t_D)$ is weaker, $n = 0.5$; as the sand grains become smaller the dependence $D^*(t_D)$ on the initial section of the curve becomes stronger and n increases to 0.7.

We note that this tendency for the observed exponent n to increase with increasing obstacle sizes for a fixed time interval t_D is consistent with the theoretical prediction (23). Indeed, the relation (23) was derived for quite short times t_D, satisfying the relation (21). For long times $t_D \gg r_0^2/D_0$ the time dependence of the correlation function is given by

$$\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^* \propto t_D^{-1},$$

which can be easily seen from the relation (14) and the fact that $\lim_{t_D \to \infty} D^*(t_D) = D^* = \text{const}$, where D^* is the self-diffusion coefficient in a random medium.[11]

Hence it is clear that the measured value of the exponent $n = 0.7$ for specimens Nos. 2 and 3 is related with the fact that the time t_D, whose lower limit is the dead time of the apparatus, does not satisfy as well the condition that it be small. It seems to us, however, that the agreement itself between the measured dependences of the autocorrelation function of the force of interaction of a molecule with the surface of the porous system on the time t_D and the theoretical estimate (23) is satisfactory.

We discuss now the absolute magnitude of the autocorrelation function $\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^*$ for $t_D = 3$ ms. As one can see from Table I,

$$\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^* \sim 10^{-30}\ \mathrm{H}^2.$$

This quantity is approximately six to seven orders of magnitude smaller than the squared force of the characteristic interaction of two molecules $f_{\mathrm{mol}}^2 \approx (k_B T/d)^2 \sim 10^{-23}\mathrm{N}^2$, where d is of the order of the intermolecular distance. This ratio of these quantities is reasonable.

Indeed, over a time of the order of $t_D = 3$ ms a molecule initially located at the wall of the porous material moves away from the wall to a distance of the order of $\sqrt{(D_0 t_D)} \approx 10^4$ Å. The smallness of the quantity $\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^*/f_{\mathrm{mol}}^2$ reflects the fact that the total residence time t_1 of a molecule at the wall is short compared with the diffusion time t_D [see formulas (18)–(23)].

This is a good point at which to indicate the following circumstance. From time to time the possibility of the existence, on the boundary with the surface of the porous material, of surface layers of liquid with thicknesses of the order of 10^3–10^4 Å and structurally different from the main liquid is discussed in the literature (see, for example, Refs. 15 and 16). The above estimates of the ratio $\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^*/f_{\mathrm{mol}}^2 \approx 10^{-6}$–$10^{-7}$ can be considered to be direct experimental evidence of the absence of any serious changes in the structure of the liquid over these spatial scales in systems of the type sand-tridecane which we studied.

It follows from the relation (23) that the correlation

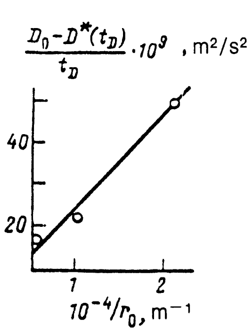

FIG. 4. Parameter $(D_0 - D^*(t_D))/t_D$ as a function of the inverse radius of the sand grains in specimens Nos. 4, 5, and 6.

function $\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^*$ is inversely proportional to the radii r_0 of the obstacles. Figure 4 shows the experimentally measured dependence of this function on the radii of the sand grains for specimens Nos. 4 and 5, in which the concentration of the liquid is almost constant (see Table I). The value of the correlation function was taken at $t_D = 3$ ms. It is clear that the correspondence with the theoretical estimate (23) is satisfactory in this case also.

It is interesting to estimate, on the basis of the relations (23) and (14), from the experimental data the ratio of the "settled" lifetime τ_1 on the surface of the porous material to the "settled" lifetime τ_0 in the pure liquid with the help of the relation

$$\frac{\tau_1}{\tau_0} \approx \frac{D_0-D^*(t_D)}{D_0}\,\frac{r_0}{(D_0t_D)^{1/2}}\,\frac{1}{n\Gamma(2+1/n)}\,\frac{1-\varphi}{\varphi}. \qquad (25)$$

The average values of this ratio, which were determined from the experimental data in the time interval $t_D = 5$–100 ms with $n = 10$, are presented in the last column of Table I.

We note first that an estimate based on the formula (25) gives only the order of magnitude, since we do not know the numerical coefficient which was omitted from relation (23). Nonetheless it is less comforting that all these numbers have turned out to be quite close to one another. The systematic increase of these numbers with decreasing radii of the sand grains is probably related with the fact, mentioned in the discussion of the formula (24), that the condition (21) that t_D be small for systems with small obstacles is not as well satisfied. The fact that the ratio $\tau_1/\tau_0 < 1$ seems to be associated with the fact that on the whole the obstacles repel molecules. It is thus natural that the "settled" lifetime at the surface is shorter than the "settled" lifetime in a pure liquid. Of course, these assertions will be much more reliable after the temperature dependence of the ratio τ_1/τ_0, determined from the experimental data with the help of the formula (25), is carefully analyzed. It seems to us that such investigations are a very useful scientific problem. We also note that in the derivation of the relation (23) the potential (15) describing the interaction of a molecule with the wall of the porous system was assumed to be repulsive. For this reason, we can state that our experimental data on the possible values of the ratio τ_1/τ_0 are consistent with the theoretical predictions (23).

The concentration dependence of the correlation function $\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^*$ was studied with specimens Nos. 3 and 4 as the example. It was found that the ratio of the correlation functions for $t_D = 3$ ms calculated for the indicated specimens with the help of the formula (23) was equal to 1.74, while the experimentally determined value of this ratio is equal to 1.45.

We begin our discussion of these numbers from the fact that as far as the concentration dependence is concerned the agreement between the expression (23), describing an idealized model, and a real porous tridecane-sandstone system should not be as good. This is connected primarily with the fact that, as indicated in Sec. 2 of this paper, liquid does not completely fill the pores of the sandstone. The remaining voids act as additional obstacles, since, owing to surface tension, the molecules of the liquid are on the whole reflected from the liquid-gas boundary. Hence it is obvious that interactions on this boundary also contribute to the correlation function $\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^*$, and this was neglected in the derivation of the formula (23). It is clear that these corrections affect primarily the concentration dependence of the correlation function $\langle \mathbf{f}(t_D)\mathbf{f}(0)\rangle^*$. For this reason, the agreement indicated above between the theoretical concentration dependence and the experimentally observed dependence can be considered to be satisfactory.

We end this paper with the following general remark. The theoretical foundation of this paper and of Ref. 11 is Smoluchowski's equation. It is well known that this equation can be rigorously derived only in the so-called long-wavelength approximation (see, for example, Refs. 17 and 7). In general, however, it is clear that the interaction of a molecule with the surface of a porous medium is, on the whole, of a microscopic character. On the phenomenological level short-wavelength effects could be taken into account by including higher powers of the Laplacian in Eq. (5) (see Ref. 18). The results of the present work show that Smoluchowski's equation gives at least a good qualitative description of the real dynamic processes occurring in the systems studied, though undoubtedly investigation of short-wavelength effects is of scientific interest in itself.

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