ANALYSIS OF THE DIFFUSION RATE IN LIQUIDS WITHIN THE RANDOM WALK MODEL

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A description of the diffusion rate in liquids is given within the molecular random walk model. A new mathematical model is worked out and applied to find the explicit time-dependences of a mathematical expectation and the concentration of molecules at the diffusion front and to calculate new expressions for the probability density distribution functions.

Introduction

This paper does not deal with the whole variety of problems concerning Brownian motion kinetics. Instead, we consider a specific problem of how to find the most probable time-dependence of the liquid drop size in the course of diffusion in terms of the mathematical model of random walk. A model is proposed under the two assumptions, i.e., that

1) Bogolyubov's condition of correlation weakening [1] is satisfied;

2) the velocity distribution of scattered Brownian particles is homogeneous.

The rightfulness of the first condition was considered in [2]. There, it was proved that the account of correlations yields distribution functions similar to those of a system without fluctuations. The second condition is associated with the Langevin force, which is a random function of time. Our mathematical model is constructed for a special case of this function. We have chosen such statistical parameters of the Langevin force that the particle velocity distribution is homogeneous under successive scattering events.

1. Construction of the Mathematical Model

Suppose two particles are located at the points O_1 and O_2 spaced at distance l_0 at the initial (zero) time instant. At the next, unit time instant (when the initial scattering act occurs), the particle that has been initially at the point O_1 can occupy any point A_1 on sphere *1* of radius R with the point O_1 at the center with equal probability. The particle from the point O_2 can occupy, with equal probability, any point A_2 on sphere *2* of radius R with the center at the point O_2. Let us find the probability density distribution function for the unit instant of time and a finite distance l_1 between the points A_1 and A_2.

We denote this function as $G(l_0,l_1)$.

To solve the first problem, we employ the method proposed in [3]. We assume the function in question to be determined by the ratio of the measure of the set $\{m\}$ of all pairs of points (A_1, A_2) spaced at distance l_1 to the measure of the set $\{M\}$ of all pairs of points (A_1, A_2), i.e.,

$$G(l_0, l_1) = m/M. \tag{1}$$

Suppose A_1 and A_2 are arbitrary points of arbitrary overlapping spatial domains K_1 та K_2, respectively. According to [4], the measure density of the set of pairs of points A_1 and A_2 is given by

$$dM = dx_1 \wedge dy_1 \wedge dz_1 \wedge dx_2 \wedge dy_2 \wedge dz_2. \tag{2}$$

Integrating expression (2) over all probable coordinates of the points A_1 and A_2 results in

$$M = \int\limits_{K_1} dx_1 \wedge dy_1 \wedge dz_1 \int\limits_{K_2} dx_2 \wedge dy_2 \wedge dz_2 = V_{K_1} V_{K_2}, \tag{3}$$

where $V_{K_1}$and V_{K_2} are the volumes of the spatial domains K_1 and K_2, respectively.

Thus, the measure of the set $\{M\}$ of all probable pairs of points is equal to the product of the volumes of the spatial domains K_1 and K_2.

In our case, the domains K_1 and K_2 are spheres of radius R, hence the measure of the set $\{M\}$ is given by

$$M = \frac{4}{3}\pi R^3 \cdot \frac{4}{3}\pi R^3 = \frac{16}{9}\pi^2 R^6. \tag{4}$$

To calculate the measure m, we divide the procedure into two stages.

Calculation of the measure $f(x)$ of the set $\{F\}$ of all pairs of the points A_1 and A_2 spaced at l_1, with x being

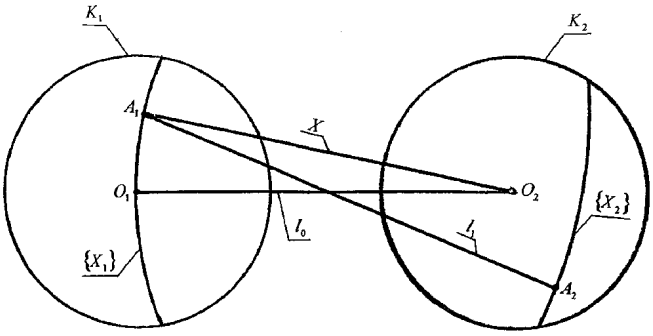

Fig. 1. Point sets $\{X_1\}$ and $\{X_2\}$ for the domains K_1 and K_2, respectively

the distance between the point A_1 and the center of sphere *2*.

Calculation of the measure m as a sum of all probable measures $f(x)$, i.e.,

$$m = \int f(x)\, dx, \tag{5}$$

where the integration extends over all probable values of x.

According to [4], the measure density of an arbitrary set of points may be presented in the form

$$df(x) = dP_1 \wedge dP_2, \tag{6}$$

where dP_1 is the measure density of the set $\{X_1\}$ of the points A_1 spaced at distance x from the center of sphere *2*, and dP_2 is the measure density of the set $\{X_2\}$ of the points A_2 spaced from an arbitrary fixed point of the set $\{X_1\}$ at distance l_1. Fig. 1 gives an example of the sets $\{X_1\}$ and $\{X_2\}$.

We integrate Eq. (25) over the point set $\{X_2\}$, i.e.,

$$\int\limits_{\{X_2\}} df(x) = dP_1 \int\limits_{\{X_2\}} dP_2. \tag{7}$$

The set $\{X_2\}$ is a connected surface domain of the sphere W_2 of radius l_1 with the center at an arbitrary fixed point of the set $\{X_1\}$ positioned within sphere *2*. According to [4], the measure of the set of all points of a connected surface domain is the area of this domain.

Therefore, the integral on the right-hand part of Eq. (7), which is the measure of the set $\{X_2\}$, is equal to the area of the domain W_2 that lies within sphere *2*.

Having denoted this area by $S_2(x)$, we rewrite Eq. (7) as

$$\int\limits_{\{X_2\}} df(x) = S_2(x)\, dP_1. \tag{8}$$

We integrate both parts of Eq. (28) over the set $\{X_1\}$, then the left-hand part of Eq. (28) is equal to the measure of the point set $\{F\}$, i.e.,

$$f(x) = \int\limits_{\{X_1\}} \int\limits_{\{X_2\}} df(x). \tag{9}$$

Inasmuch as the area $S_2(x)$ is the same for all points of the set $\{X_1\}$, we can put it before the integration symbol and thus the result is reduced to

$$f(x) = S_2(x) \int\limits_{\{X_1\}} dP_1. \tag{10}$$

The set $\{X_1\}$ is a connected surface domain of the sphere W_1 of radius x with the center at the point O_2 that lies within sphere *1*. Hence the integral on the right-hand part of Eq. (10) is equal to the area of the domain W_1. With this area being denoted by $S_1(x)$, we write Eq. (10) as

$$f(x) = S_1(x)\, S_2(x). \tag{11}$$

Integrating Eq. (11) over all probable values of x yields the measure m of the set $\{m\}$. Having substituted the obtained expression in (1), we find an expression for the function $G(l_0, l_1)$ that is different for different values of l_0 and l_1. Thus, we get

$$\begin{aligned}
&1.\ G(l_0,l_1) = 0, \text{ for } l_0 > 2R,\ l_1 > l_0 + 2R.\\
&2.\ G(l_0,l_1) = G_1, \text{ for } l_0 \geq 2R,\ l_0 \leq l_1 \leq l_0 + 2R.\\
&3.\ G(l_0,l_1) = G_2, \text{ for } l_0 \geq 2R,\ l_0 - 2R \leq l_1 \leq l_0.\\
&4.\ G(l_0,l_1) = 0, \text{ for } l_0 \geq 2R,\ l_1 < l_0 - 2R.\\
&5.\ G(l_0,l_1) = 0, \text{ for } R \leq l_0 \leq 2R,\ l_1 > l_0 + 2R.\\
&6.\ G(l_0,l_1) = G_1, \text{ for } R \leq l_0 \leq 2R,\ l_0 \leq l_1 \leq l_0 + 2R.\\
&7.\ G(l_0,l_1) = G_2, \text{ for } R \leq l_0 \leq 2R,\ 2R - l_0 \leq l_1 < l_0.\\
&8.\ G(l_0,l_1) = G_3, \text{ for } R \leq l_0 \leq 2R,\ 0 \leq l_1 \leq 2R - l_0.\\
&9.\ G(l_0,l_1) = 0, \text{ for } 0 \leq l_0 < R,\ l_1 > l_0 + 2R.\\
&10.\ G(l_0,l_1) = G_1, \text{ for } 0 \leq l_0 < R,\\
&\qquad 2R - l_0 \leq l_1 \leq 2R + l_0.\\
&11.\ G(l_0,l_1) = G_4, \text{ for } 0 \leq l_0 < R,\ l_0 \leq l_1 < 2R - l_0.\\
&12.\ G(l_0,l_1) = G_3, \text{ for } 0 \leq l_0 < R,\ 0 \leq l_1 < l_0.
\end{aligned} \tag{12}$$

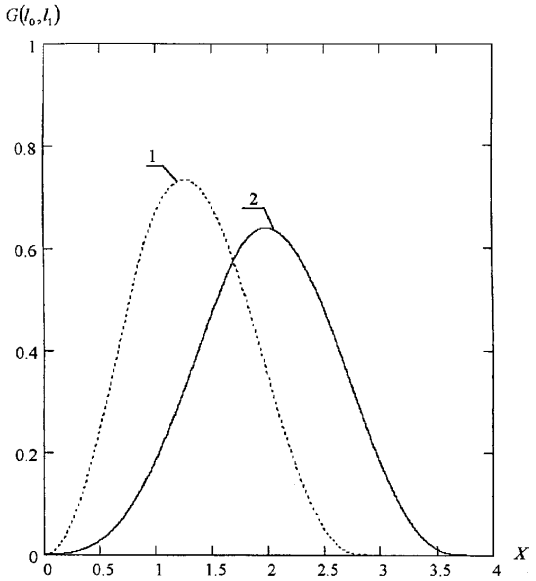

Fig. 2. Function $G(l_0, l_1)$ versus the dimensionless parameter $x = \frac{l_1}{R}$. The initial distances are $l_0 = 0.875R$ for (*1*); $l_0 = 1.75R$ for (*2*)

The functions G_1, G_2 , G_3 , G_4 are given by

$$G_1 = \frac{9}{16l_0R^6}\left\{-\frac{1}{30}l_1^6 + \frac{1}{6}l_1^5 l_0 + l_1^4\left(-\frac{1}{3}l_0^2 + \frac{2}{3}R^2\right) + \right.$$

$$+l_1^3\left(\frac{1}{3}l_0^3 - 2l_0R^2 - \frac{4}{3}R^3\right) +$$

$$+l_1^2\left(-\frac{1}{6}l_0^4 + 2l_0^2R^2 + \frac{8}{3}l_0R^3\right) +$$

$$\left.+l_1\left(\frac{1}{30}l_0^5 - \frac{2}{3}l_0^3R^2 - \frac{4}{3}l_0^2R^3 + \frac{16}{15}R^5\right)\right\}, \qquad (13)$$

$$G_2 = \frac{9}{16l_0R^6}\left\{\frac{1}{30}l_1^6 - \frac{1}{6}l_1^5 l_0 + l_1^4\left(\frac{1}{3}l_0^2 - \frac{2}{3}R^2\right) + \right.$$

$$+l_1^3\left(-\frac{1}{3}l_0^3 + 2l_0R^2 - \frac{4}{3}R^3\right) +$$

$$+l_1^2\left(\frac{1}{6}l_0^4 - 2l_0^2R^2 + \frac{8}{3}l_0R^3\right) +$$

$$\left.+l_1\left(-\frac{1}{30}l_0^5 + \frac{2}{3}l_0^3R^2 - \frac{4}{3}l_0^2R^3 + \frac{16}{15}R^5\right)\right\}, \qquad (14)$$

$$G_3 = \frac{9}{16l_0R^6}\left\{\frac{1}{15}l_1^6 + l_1^4\left(\frac{2}{3}l_0^2 - \frac{4}{3}R^2\right) + \right.$$

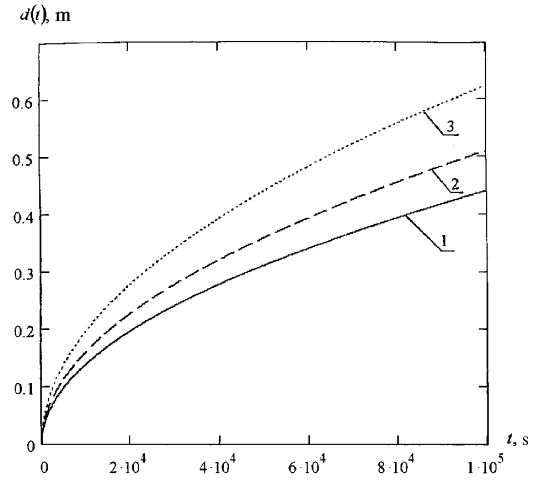

Fig. 3. Diameter d of a liquid drop as a function of time for the molecular velocities (m/s): 250 (*1*); 330 (*2*); 500 (*3*)

$$\left.+l_1^2\left(\frac{1}{3}l_0^4 - 4l_0^2R^2 + \frac{16}{3}l_0R^3\right)\right\}, \qquad (15)$$

$$G_4 = \frac{9}{16R^6}\left\{\frac{1}{3}l_1^5 + l_1^3\left(\frac{2}{3}l_0^2 - 4R^2\right) + \frac{16}{3}l_1^2R^3 + \right.$$

$$\left.+l_1\left(\frac{1}{15}l_0^4 - \frac{4}{3}l_0^2R^2\right)\right\}. \qquad (16)$$

It is not difficult to verify by a straightforward calculation that, in all the above cases, the function $G(l_0, l_1)$ satisfies the normalization condition

$$\int_{-\infty}^{+\infty} G(l_0, l_1)dl_1 = 1. \qquad (17)$$

In Fig. 3, the function $G(l_0, l_1)$ is plotted for various initial distances.

We make use of expressions (13)—(16) to find the mathematical expectation $r(1, l_0)$ for the distance l_1 between the points at the unit instant of time. Thus, we have

$$r(1, l_0) = l_0 + \frac{2R^2}{5l_0} \text{ for } l_0 > 2R, \qquad (18)$$

$$r(1, l_0) = -\frac{1}{4480}\cdot\frac{l_0^7}{R^6} + \frac{1}{80}\cdot\frac{l_0^5}{R^4} - \frac{1}{20}\cdot\frac{l_0^4}{R^3} +$$

$$+\frac{2}{5}\cdot\frac{l_0^2}{R} + \frac{36}{35}R, \quad \text{for } 0 \le l_0 \le 2R. \qquad (19)$$

Suppose some material point occupies the spatial point A_0 at the initial (zero) time instant.

At the unit time instant, it can be at an arbitrary point A_1 of the sphere of radius R with the center at

the point A_0 with equal probability. At the next time instant, it can be at any point A_2 of the sphere of radius R with the center at the point A_1 with equal probability, and so on until the time instant n. Let us find the probability density distribution function for the distance between the points A_0 and A_n.

In a manner similar to the previous analysis, we found the probability density distribution function for the unit time instant as

$$\rho(l_0,l_1)=\frac{3l_1^2}{R^3}\,\theta(R-l_0-l_1)+\frac{3l_1}{4R^3l_0}\Big(-l_1^2+$$

$$+2l_1l_0-l_0^2\Big)\theta\left(R^2-(l_1-l_0)^2\right)\theta(l_1+l_0-R). \qquad (20)$$

Suppose $l_0,l_1,...,l_n$ are arbitrary fixed distances between the points at time instants $0,1,\ldots,n$, respectively. Inasmuch as all displacements are independent, the density distribution function is equal to an integral of the product $\rho(l_0,l_1)\,\rho(l_1,l_2)...\rho(l_{n-1},l_n)$ over all probable values of $l_1,l_2,...l_{n-1}$, where $l_0=0$. Let the function of interest be denoted by $P(l_n)$, then the expression for this function is given by

$$P(l_n)=\int\limits_{L(1)}^{S(1)}\int\limits_{L(2)}^{S(2)}...\int\limits_{L(k)}^{S(k)}...\int\limits_{L(n-1)}^{S(n-1)}\prod_{k=0}^{n-1}\{\rho(l_k,l_{k+1})\}\times$$

$$\times dl_{n-1}...dl_k...dl_2dl_1, \qquad (21)$$

where $L(1)=(l_2-R)\,\theta\{l_2-R\}$, $L(2)=(l_3-R)\times$ $\times\theta\{l_3-R\}$, ..., $L_{n-1}=(l_n-R)\,\theta\{l_n-R\}$, $S_1=R$, $S_2=2R\theta\{l_3-R\}+(l_3+R)\,\theta\{R-l_3\},\ldots,$ $S_{n-1}=(n-1)\,R\theta\{l_n-(n-2)\,R\}+(l_n+R)\,\theta\{R\,(n-2)-l_n\}$. Thus, we have obtained the solution in the integral form. We have managed to perform integration only for the special case $(n-2)\,R<l_n<nR$ and have obtained

$$P(l_n)=\frac{3^nl_n}{4^{n-1}R^{3n}}\times$$

$$\times\int\limits_{l_2-R}^{R}\int\limits_{l_3-R}^{2R}...\int\limits_{l_n-R}^{(n-1)R}l_1\prod_{k=1}^{n-1}\left\{R^2-(l_{k+1}-l_k)^2\right\}\times$$

$$\times dl_{n-1}...dl_2dl_1. \qquad (22)$$

Integrating (22) yields

$$P(l_n)=\frac{3^nl_n}{2^{n-1}R^{3n}}\times$$

$$\times\sum_{j=0}^{n-1}\frac{(-1)^j\,C_{n-1}^j\,R^{n-1-j}\,(R\,(n-1+j)+l_n)}{(2n-1+j)!}\times$$

$$\times\,(nR-l_n)^{2n-2+j}, \qquad (23)$$

where C_{n-1}^j is the number of combinations.

For other cases, the function of interest can be obtained by means of numerical integration.

Let us find the density distribution function in the case where, at time instant n, l_n is the distance between two particles which have been initially spaced to the distance l_0.

Let $H(l_0,l_n)$ denote the function of interest. The integral expression of this function is given by

$$H(l_0,l_n)=\int\limits_{X(1)}^{Y(1)}\int\limits_{X(2)}^{Y(2)}...\int\limits_{X(n-1)}^{Y(n-1)}\prod_{k=0}^{n-1}G(l_k,l_{k+1})\times$$

$$\times dl_{n-1}...dl_2dl_1, \qquad (24)$$

where $X(1)=(l_2-2R)\theta\{l_2-2R\}$, $X(2)=(l_3-2R)\times$ $\times\theta\{l_3-2R\},\ldots,X(n-1)=(l_n-2R)\theta\{l_{n-2R}\}$, $Y(1)=$ $=l_0+2R, Y(2)=(l_0+4R)\theta\{l_3-l_0-2R\}+(l_3+2R)\theta\{l_0+$ $+2R-l_3\},\ldots,Y(n-1)=(l_0+2R(n-1))\,\theta\,\{l_n-l_0-$ $-2R(n-2)\}+(l_n+2R)\theta\{l_0+2R(n-2)-l_n\}$.
The solution thus obtained provides a possibility to perform the numerical integration. A detailed analysis will be given elsewhere.

Now let us consider the problem on the diffusion rate in a liquid.

2. Obtaining the Diffusion Rate Characteristics within the Developed Mathematical Model

With a drop of liquid 2 being put into liquid *1*, the volume occupied by molecules of liquid *2* increases with time due to chaotic Brownian motion of molecules. Let us find: 1) the time dependence of the diameter of a drop of liquid *2* under the assumption that there are no external forces, i.e., the mathematical expectation for the diameter, and 2) the time-dependence of the concentration of molecules of liquid *2* in the boundary layer between the spatial domain involved in the diffusion and the domain where diffusion still does not occur.

As distinct from gases, molecules of a liquid manifest short-range-order arrangement. That is why a molecule, before being scattered, can be displaced from its initial position to a distance not longer than the mean distance between molecules. This observation provides

a possibility to apply the model proposed above and to find the time-dependence of the drop diameter:

$$d = \sqrt{d_0^2 + \frac{7}{9}R\overline{u}t + \frac{R^2}{5}\ln\left\{1 + \frac{7R\overline{u}t}{9d_0^2}\right\}}, \qquad (25)$$

where d_0 is the initial diameter of the drop of liquid *2*, d is its final diameter, R is the mean distance between the molecules, $\overline{u}$ is the arithmetic mean velocity of molecules, t is the diffusion time. Fig. 3 illustrates an example of the dependence $d(t)$.

The time-dependence of the concentration of liquid *2* molecules in the diffusion boundary layer can be found by means of a simple calculation with the use of formula (23). We thus have

$$n = n_0\left(1 + \frac{2t\overline{u}}{e^{3/2}R}\right)^{-\frac{8t\overline{u}}{3R}}, \qquad (26)$$

where n_0 is the initial concentration of molecules in a drop of liquid *2*. Fig. 4 shows an example of the dependence $n(t)$.

3. Results

We have proposed a mathematical model that described the evolution of a physical system with chaotic random motion of constituent particles. For the function $G(l_0, l_1)$, the limiting case $l_0 = 0$ has already been described in the literature. The expression derived within our model for this case reproduces the function obtained in [4], i.e.,

$$G(0, l_1) = \frac{3}{16R^6}\left(l_1^5 - 12l_1^3R^2 + 16l_1^2R^3\right). \qquad (27)$$

The proposed model was applied to obtain the time dependence of the diameter of a liquid *2* drop, which diffuses in liquid *1*, with higher accuracy than the expressions known from the literature. In the limiting case, the dependence obtained reproduces the results published before, e.g., in [5]. The concentration of molecules of a liquid at the diffusion front is estimated as well. This result should be verified experimentally.

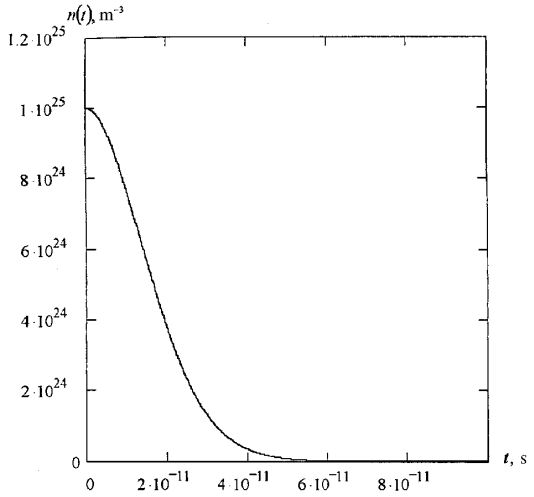

Fig. 4. Concentration of molecules at the diffusion front as a function of time, $n(t)$, for $n_0 = 10^{25}\ m^{-3}$, $\bar{u} = 500$ m/s

1. *Bogolyubov N.N.* Problems of Dynamical Theory in Statistical Physics. – Moscow–Leningrad: Gostekhizdat, 1946 (in Russian).
2. *Peletminsky S.V., Sokolovsky A.I.*// Ukr. Fiz. Zh. – 1992. – **37**, N 10. – P.1521 – 1528.
3. *Santalo L.A.* Introduction to Integral Geometry. – Paris: Hermann, 1953.
4. *Santalo L.A.* Integral Geometry and Geometric Probabilities. – Reading: Addison –Wesley, 1979.
5. *Klimontovich Yu.V.* Statistical Physics. – Moscow: Nauka, 1982 (in Russian).

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АНАЛІЗ ШВИДКОСТІ ПРОТІКАННЯ ДИФУЗІЇ У РІДИНІ З ВИКОРИСТАННЯМ МАТЕМАТИЧНОЇ МОДЕЛІ ВИПАДКОВИХ БЛУКАНЬ

К.В. Авдонін

Р е з ю м е

Досліджено питання про можливість визначення швидкості протікання дифузії у рідині на базі математичної моделі випадкових блукань молекул рідини. За допомогою побудованої в роботі математичної моделі знайдено явні залежності математичного сподівання та концентрації молекул для фронту дифузії від часу. Отримано нові функції розподілу для моделі випадковоих блукань молекул рідини.