

Non-Classical Diffusion in Dense Gases and Liquids

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Abstract. The diffusion of molecules in liquids and dense gases is demonstrated to be nonclassical for long time intervals. This means that the time dependence of the mean-square displacement of molecules is nonlinear. This result was obtained by molecular dynamics simulations for a wide range of density of the medium. The problem of plateau values of the diffusion coefficient is discussed. A nonclassical diffusion equation is derived.

Keywords: diffusion, non-classical diffusion, dense gases, liquids, velocity autocorrelation function, molecular dynamics method.

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INTRODUCTION

In his classical paper [1], Einstein showed that the mean-square displacement $\langle R^2(t) \rangle$ of Brownian particles in liquids has the linear time dependence

$$\langle R^2(t) \rangle = 6Dt \quad (1)$$

where D is the diffusion coefficient (the angle brackets denote the average value). Ever since it has been assumed that the diffusion of molecules of gases and liquids is also described by relation (1).

Formula (1) is a consequence of Einstein's assumption that the coordinate distribution function of Brownian particles $\Psi(\mathbf{r}, t)$ satisfies the local diffusion equation

$$\partial \Psi(\mathbf{r}, t) / \partial t = D \nabla^2 \Psi(\mathbf{r}, t). \quad (2)$$

This implies that the particle motion is a Gaussian and Markov process or, more precisely, a Wiener process. From the point of view of Langevin's theory, the motion of Brownian particles is also defined as a Gaussian and Markov process but it is a stationary stochastic process (an Ornstein–Uhlenbeck process). The particle velocity \mathbf{v} satisfies the Langevin equation

$$\dot{\mathbf{v}} = -\gamma \mathbf{v} + \mathbf{f}(t), \quad (3)$$

where γ is the drag coefficient and $\mathbf{f}(t)$ is the stochastic force. Therefore, the velocity autocorrelation function (VACF) $\chi_{vv}(t) = \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$ of a particle decreases exponentially

$$\chi_{vv}(0, t) = \langle \mathbf{v}^2(t) \rangle \exp(-t / \tau), \quad (4)$$

where τ is the relaxation time.

However, the dynamics of Brownian particles does not have Markov properties, and Eq. (1) is applicable only when $t \gg \tau$. In addition, for dense gases and liquids, relation (1) is not correct for small distances (see, for example [2]). In fact, the VACF of rarefied-gas molecules decreases exponentially, and the diffusion of these molecules is described by Eq. (1). In all other cases (namely, in dense gases and liquids), the VACF has the slow long-time asymptotics $\chi_{vv} \sim t^{-3/2}$ [3]. It is apparent that the molecule velocity in this case is not described by Eq. (3). The main objective of this study is to answer the question of whether the diffusion of molecules is defined by Eq. (1).

TIME DEPENDENCE OF THE MEAN-SQUARE DISPLACEMENT OF MOLECULES IN FLUIDS

The mean-square displacement of a molecule in a time interval t is related to its VACF by the formula [4]

$$\langle R^2(t) \rangle = \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle = 6 \int_0^t (t-s) \chi_{vv}(s) ds. \quad (5)$$

We can substitute the VACF (4) into the right side of Eq. (5) and take the limit $t \gg \tau$, where τ is the mean free time of the molecule. As a result, we obtain the Einstein law (1). As noted above, for dense gases and liquids, the VACF has a “long-time tail.” Hard-sphere molecular dynamics calculations have shown [5] that this tail is described by the function

$$\chi_{vv}(0, t) = \langle \mathbf{v}^2(t) \rangle = \left[\exp(-t/\tau) + B(t - t_*)^{-\frac{3}{2}} \right]. \quad (6)$$

where all times are dimensionless and are measured in units of the mean free time of the molecules.

This approximation was calculated for 27000 molecules in a modelling cell. The dependence of the parameters B and t_* on density is presented in Table 1. Here $\alpha = V/V_0$, V is the volume of the system, $V_0 = N\sigma^3/\sqrt{2}$ is the close-packed volume, N is the number of molecules in the cell, and σ is the molecule diameter.

TABLE 1. Parameters of approximation (6).

α	2	3	5	10
t_*	0.48	2.87	4.91	7.54
B	0.54	0.37	0.132	0.021

Substituting expression (6) into Eq. (5) and integrating the latter, we have the relation

$$\langle R^2(t \gg \tau) \rangle = 6Dt \left(1 - 4Bt^{-1/2} \right) = I_1 - I_2. \quad (7)$$

Thus, the diffusion of molecules of liquids and sufficiently dense gases is nonclassical. It should be noted that the corrections due to the second term in expression (7) are negligibly small only for moderate-density gases. Curves of the function $\gamma = I_2/I_1$ versus the time $t' = t/\tau$ for fluids of various densities are presented in Fig. 1. Here curves 1, 2, 3, and 4 correspond to density values $\alpha = 2, 3, 5$, and 10, respectively. Obviously, the contribution of I_2 decreases with increasing time. It is about one percent for dense gases or several percent for liquids (see Fig. 1). This contribution is appreciable even for $t = 2000\tau$. The kinetic stage of the evolution of the molecular system has a duration on the order of τ ; it is therefore clear that nonclassical molecular diffusion is observed at the times corresponding to the hydrodynamic stage.

The difference between the real diffusion law (7) and the classical one (1) has practical importance because relation (7) is the basis of methods for measuring both molecular diffusion coefficients and self-diffusion coefficients. In principle, this limits the accuracy of measurements of molecular diffusivity in dense gases and liquids.

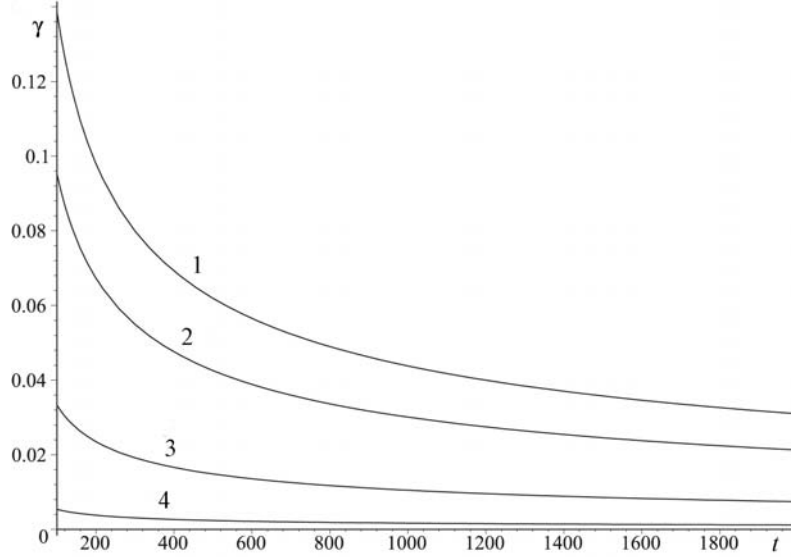


FIGURE 1. Time dependence of the parameter $\gamma = I_2 / I_1$ for fluids of various densities.

Expression (1) is frequently used in molecular-dynamics calculations of diffusion coefficients (see, for example, [6]). From Fig. 1 one can see that it leads to significant errors. It was also obtained directly by molecular-dynamics calculations. We performed accurate calculations of the function $\langle R^2(t) \rangle$. The calculation result is shown in Fig. 2 for a density value $\alpha = 2$). Here the dotted curve is the molecular-dynamics calculation and the solid curve is its approximation by the linear relation (1). It is found that if the condition $t \gg \tau$ is satisfied (the calculations were carried out in the interval from 200 to 400 τ and for $N = 27000$), the approximation of the function $\langle R^2(t) \rangle$ by the linear function (1) is significantly worse (by approximately 3 %) than the approximation by the function $6Dt(1 - A/\sqrt{t})$.

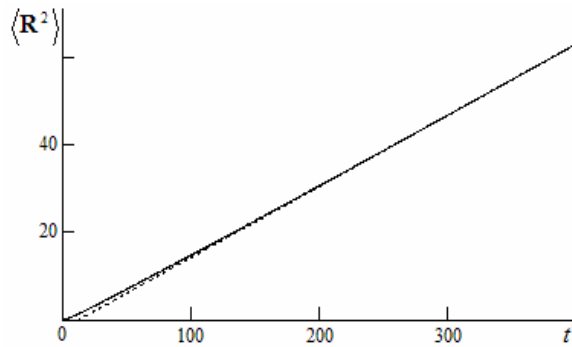


FIGURE 2. Time dependence of the mean-square displacement.

ABOUT THE PLATEAU PROBLEM FOR TRANSPORT COEFFICIENTS IN STATISTICAL MECHANICS

In the previous section, we established that the diffusion of fluid molecules exhibits a nonclassical behaviour. Nevertheless, taking the limit as $t \rightarrow \infty$, we obtain

$$D = \lim_{t \rightarrow \infty} \langle R^2(t) \rangle / 6t. \quad (8)$$

One can say that the second nonclassical term in expression (8) is of no practical importance. However, the situation is a bit more subtle. It is true that $\langle R^2(t) \rangle$ is limited by the size of the system for arbitrary finite molecular systems. Therefore, the limit (8) is generally equal to zero. A similar result is obtained when the diffusion coefficient is calculated using the Green–Kubo formula

$$D = \frac{1}{3} \int_0^\infty \chi_{vv}(t) dt \quad (9)$$

We have the famous “stumbling block” of modern statistical mechanics, which is usually solved by passing to the thermodynamic limit in Eqs. (8), (9) (see, for example, [4]). We suppose that a theory which requires the use of the infinite limit has serious disadvantages. There is another possibility. It is not necessary to pass to the infinite limit in the Green–Kubo formula (9) if there is the finite time T_p defined by the condition that the integral value is time independent when $t > T_p$. This period of time is the plateau time, and the corresponding value of integral (9) was called the plateau value. When this period of time exists, the mathematical limit $t \rightarrow \infty$ can be replaced by the physical limit $t \gg \tau$.

The finite limit of integration for calculations of the drag coefficient of Brownian particles was first introduced by Kirkwood [7]. The existence of the plateau values of the transport coefficient is one of the fundamental problems of modern statistical mechanics. In the 1960s and 1970s, it was discussed widely but this problem has not been solved. The plateau values have not been found by molecular-dynamics calculations because such calculations require a large number of molecules in the cell and calculation times of the order of thousands of mean free times.

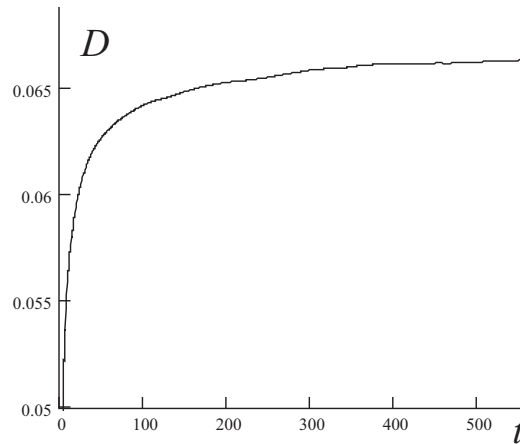


FIGURE 3. Time dependence of the self-diffusion coefficient for $N = 27000$.

Similar computations were carried out by the authors with colleagues [5]. As an example, Fig. 3 shows the time dependence of the self-diffusion coefficient (the measurement units are σ/τ_0 , $\tau_0 = \sigma/\sqrt{\langle v^2 \rangle}$) for a liquid of density $\alpha = 2$. It is evident from the figure that the plateau value is reached in a time of about 350τ . It is found that

the difference between the values of the self-diffusion coefficient calculated for times of 100τ and 350τ exceeds 3%.

The transport coefficients are integrals of the correlation functions of some dynamical variables. Therefore, the existence of the plateau values implies that starting from a certain time, these correlation functions near the zero value behave as almost periodic functions. Validation of this fact follows from papers [8].

In molecular-dynamics calculations, the values of the VACF of molecules for rather long times are very small and are significantly influenced by statistical fluctuations. However, Fig. 4 shows that the VACF ($\psi = \chi_{vv}(0, t) / \langle \mathbf{v}^2(t) \rangle$) alternatively takes positive and negative values. Statistical errors do not exceed 0.01 % of the value of $\psi(0)$.

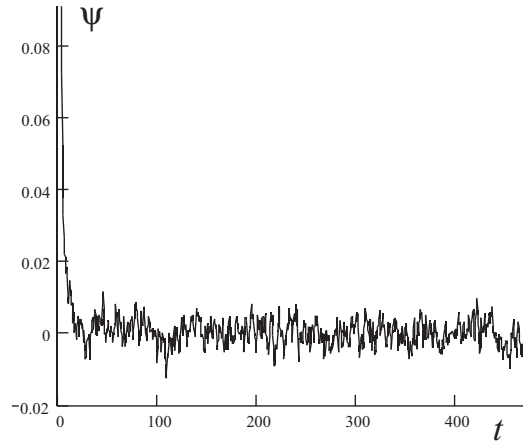


FIGURE 4. Evolution of the dimensionless VACF for $N = 27000$ and $\alpha = 2$.

POSSIBLE NON-CLASSICAL DIFFUSION EQUATIONS

The existence of long-time tails of the VACF makes it necessary to investigate the range of validity of the classical local transport equation. As an example, we consider the diffusion equation for a multicomponent fluid. For simplicity, we consider an isothermal system whose mean mass velocity is equal to zero. In this case, the dynamics of the concentration n is described by the equation

$$\partial n / \partial t = -\nabla \cdot \mathbf{J} . \quad (10)$$

If the mass flux is proportional to the concentration gradient, $\mathbf{J} = -D\nabla n$, with a constant diffusion coefficient D , we have Fick's law and Eq. (10) reduces to the ordinary diffusion equation. However, the transport processes are generally nonlocal. In particular, if we take into account only the time nonlocality (memory effects), the mass flux is given by the relation

$$\mathbf{J}(t) = -\int_{t_0}^t dt' N(t-t') \nabla n(t') , \quad (11)$$

The relaxation transport kernel $N(t-t')$ is determined by the VACF of molecules of the corresponding type. In continuum mechanics, it is modelled by the δ -function $N(t-t') = D\delta(t-t')$. Fick's law is obtained in just this case. The relaxation time related to kinetic processes in dense gases and liquids is indeed very small; therefore, the first term of expression (11) can be modelled by the δ -function. The second term in (11) is due to collective hydrodynamic relaxation processes and it damps in periods of time of the order of hundreds of mean free times of

molecules. Taking into account this fact and assuming that the concentration gradient varies slowly in these periods of time, we can write the mass flux as

$$\mathbf{J}(t) = -\tilde{D}\nabla n(t) + \frac{\tilde{B}}{(t-t_*)^{1/2}}\nabla n(t), \quad (12)$$

where \tilde{D} and \tilde{B} are new constants.

The solution of the corresponding diffusion equation with a δ -type initial density has the form

$$n(\mathbf{r}, \tau) = \frac{n(\mathbf{r}, 0)}{\left[4\pi(D\tau - D_1\sqrt{\tau})\right]^{3/2}} \exp\left[-\frac{r^2}{4(D\tau - 2D_1\sqrt{\tau})}\right]. \quad (13)$$

This distribution differs from the ordinary Gaussian distribution when the period of time is not so long.

In principle, the existence of the long-time tail can be treated as a certain relaxation source. In this case, it is necessary to use the mean-value theorem to calculate the flux (11). As a result, we have

$$\mathbf{J}(t) = -\tilde{D}\nabla n(t) + \nu(t-t_*)^{-1/2}, \quad (14)$$

where ν is a function of space variables. The corresponding diffusion equation has the form

$$\partial n / \partial \tau = \tilde{D}\nabla^2 n - \frac{\nu}{\tau^{1/2}}. \quad (15)$$

In conclusion, we note that the nonclassical diffusion is referred to as anomalous diffusion. It usually occurs in systems with a fractal structure of the phase space (see, for example, [9] and the references therein). For $\langle R^2(t) \rangle \sim t^\beta$ and $\beta < 1$, there is subdiffusion, and for $\langle R^2(t) \rangle \sim t^\beta$ and $\beta > 1$, there is superdiffusion. It is possible that the diffusion (7) is the natural transition between classical diffusion and subdiffusion. There are some cases where the subdiffusion regime is described by an equation of type (15) [10].

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