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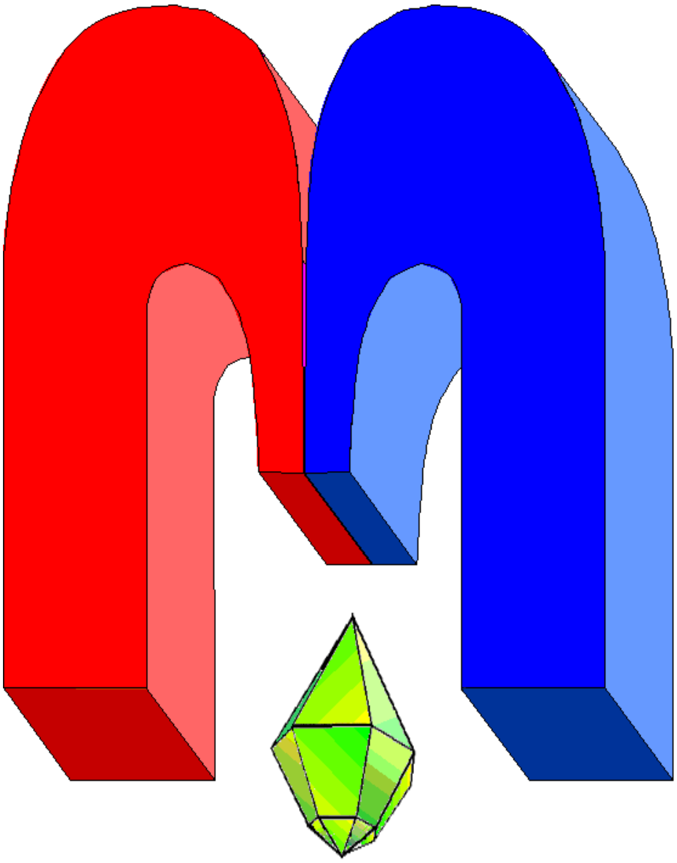

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Short-time diffusion behavior of Brownian particles in porous solids[†]

N.F. Fatkullin[1,*], R. Valiullin[2]
[1]Kazan Federal University, Kremlevskaya 18, 420008 Kazan, Russia
[2]University of Leipzig, Linnestraße 5, D-04103 Leipzig, Germany
[*]*E-mail: Nail.Fatkullin@kpfu.ru*

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The process of self-diffusion of particles confined to porous solids is studied for time intervals corresponding to particle displacements shorter than the characteristic pore size. The solid matrix is modeled as a (random) potential field with an infinitely large potential within the solid which decays to zero at distances of the order of a few particle sizes from the pore walls. Diffusion of particles in the thus created potential field is described by the Smoluchowski diffusion equation. It is shown that, for short diffusion times, the resulting equation for the time-depended diffusivity reproduces that earlier obtained in the literature [Mitra *et al.*, Phys. Rev. Lett. **68**, 3555 (1992)], but with the numerical constant differing by factor 2. The conditions under which this discrepancy arises are highlighted and discussed.

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1. Introduction

Diffusion, or erratic thermal motion of molecules, is an ubiquitous phenomenon in nature, which often plays a key role in variety of bio- or physico-chemical processes. Under equilibrium conditions and in spatially homogeneous and isotropic systems, the Green's function, i.e. the probability density to find a particle at a distance r from its origin at a time instance t, is a Gaussian function. For long enough times, this leads to the fact that the mean squared displacements $\langle r^2(t)\rangle$ grow linearly with time [1]. This regime is often referred to as normal diffusion. In many cases, however, diffusion occurs in inhomogeneous environments, with the most prominent examples being fluid transport in biological cells or porous solids. Under these conditions, some part of space becomes inaccessible for the diffusing particles, rendering the process of diffusion to deviate from the normal behavior on the length scales comparable to characteristic sizes ξ of the structural inhomogeneities. In porous media, which are in the focus of this work, ξ can be associated with typical pore sizes. In this anomalous regime of diffusion, $\langle r^r(t)\rangle \propto t^k$ with $0 < k < 1$, hence referred to as sub-diffusion (notably, k may also be a function of time). For permeable media, the normal diffusion behavior can further be recovered at length scales notably exceeding ξ. Understanding the relationships between diffusion processes and structural properties of porous materials is of particular importance for predicting molecular transport in practical applications, such as oil recovery, water infiltration, etc., and for structural characterization [2].

In a most direct way, the mean squared molecular displacements can be measured using the pulsed field gradient technique of nuclear magnetic resonance (PFG NMR) [3–5]. This method is based on the positional encoding of the spin-bearing molecules and their subsequent decoding using short pulses of magnetic field gradients. Between these two pulses, a well-controlled in

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[†]This paper is originally written by authors on the occasion of eightieth birthday of Professor Boris I. Kochelaev.

the experiment time t (also referred to as diffusion time) is given for system to evolve. If the molecules during the time interval t perform purely stochastic, translational motion, the measured signal intensity S is found to be attenuated by the factor

$$S(q,t)/S(0,t) = \exp\left\{-\frac{1}{2}q^2\langle r^2(t)\rangle\right\}, \tag{1}$$

where q is the wave number, which is controlled in the experiment. Alternatively, (1) may also be considered as a first term in the expansion in case if the Green's function cannot be approached by a Gaussian function [5]. Typically, the experimentally measured quantity $\langle r^2(t)\rangle$ is expressed in terms of the effective diffusion coefficient D_e, which is defined via the Einstein equation

$$D_e(t) = \langle r^2(t)\rangle/6t. \tag{2}$$

In PFG NMR, one typically explores diffusion processes in the time scale $10^{-3} \lesssim t \lesssim 10$ s. Hence, for low molecular liquids and on the time scale of the PFG NMR measurements, D_e, as measured using this technique and as defined by (2), turns out to be, to good accuracy, constant and to coincide with the bulk self-diffusivity D_0. In porous materials, however, D_e is found to decrease with increasing time for diffusion times $t \lesssim R^2/D_0$, where R is the characteristic pore size [6]. This behavior can easily be revealed by combining the equations (1) and (2). The time dependence of the diffusivity results from the fact that the solid matrix is impermeable for the diffusing particles, giving rise to the reflecting boundary conditions at the pore walls. One may expect, therefore, that the effective diffusivity can be a function of the surface area, at which the reflection of the particle fluxes occurs. In the context of the PFG NMR diffusion measurements of fluids in porous solids, the understanding of the relationships between the structural parameters of porous media and the time-dependent diffusivity was put forward in Refs. [7–9]. In particular, by considering the classical Fick's diffusion equation with the boundary condition posing zero gradient of the Green's function at the pore walls it was shown that, for sufficiently short diffusion times, D_e is indeed determined by the surface-to-volume ratio S/V_p of the pore space [7]:

$$D_e(t) = D_0\left(1 - \frac{4}{9}\frac{S}{V}\sqrt{\frac{D_0 t}{\pi}} + O(D_0 t)\right). \tag{3}$$

This result has further been reproduced in a number of analogous studies (see, e.g., [6, 10]). The approach based on (3) has become a robust and widely used tool for the determination of the S/V_p ratio for different porous materials by measuring the time-dependent diffusivity using PFG NMR [11–18]. It may be noted, however, that in several works an overestimation of the surface-to-volume ratio by a factor of about 2 using (3) was reported [19, 20].

The effect of the solid matrix upon diffusing particles can alternatively be described on the basis of the Smoluchowski diffusion equation [21]. In this case, the pore space and the solid are modeled as the sub-spaces with low and infinitely large potentials $U(\mathbf{r})$, respectively, with a smooth transition between them. Thus, close to the pore walls, the moving particles experience a change of the potential, which can effectively be treated as the action of a force $-\partial U(\mathbf{r})/\partial\mathbf{r}$. Diffusion of particles in the presence of a force field generated by the solid matrix, which is generally described by the Smoluchowski diffusion equation, was already considered in the literature in connection with PFG NMR experiments [22, 23]. In this work, we use this approach to study the short-time diffusion behavior of low-molecular liquids in porous materials.

Because in this way the interaction of molecules with the solid can be described on a more realistic level, the main goal of this work was to establish how it may render the results obtained earlier using classical Fick's diffusion equations.

2. Results

In this work, the influence of the solid matrix on the confined molecules was described by means of an effective random potential $U(\mathbf{r})$ induced by the heterogeneous medium. Within the solid, which effectively plays a role of obstacles for the Brownian particles, $U(\mathbf{r}) \to \infty$, while in the pore space $U(\mathbf{r}) \to 0$. At the pore walls, the potential falls to zero within the surface layer of the order of a few particle sizes. This length scale we denote by a_0 and it may be associated with the thickness of a surface layer having differen physical properties as compared to the bulk phase. In all physically relevant cases, this transition is considered to be smooth. We consider only the quenched fields $U(\mathbf{r})$, which do not vary in time, i.e., the molecular or particle mass is considered to be negligibly small as compared to the mass of the solid, thus the motion of the latter can be ignored.

The probability density $W(\mathbf{r};t)$ for the molecular displacements, namely the Green's function, satisfies the Smoluchowski equation

$$\frac{\partial}{\partial t} W(\mathbf{r};t) = D_0 \frac{\partial}{\partial \mathbf{r}} \left[\frac{\partial}{\partial \mathbf{r}} - \frac{1}{kT} \mathbf{f}(\mathbf{r}) \right] W(\mathbf{r};t), \tag{4}$$

where D_0 is the diffusivity in the bulk liquid, $\mathbf{f} = -\partial U(\mathbf{r})/\partial \mathbf{r}$ is the force induced by the random potential, k is the Boltzmann constant, and T is temperature. Note that the differential operator on the right hand side of (4) is not a self-adjoint one. This makes the problem rather complex from the mathematical point of view. To simplify the problem, we introduce a new function $\Psi(\mathbf{r},t)$ which is related to $W(\mathbf{r},t)$ via

$$\Psi(\mathbf{r},t) = W(\mathbf{r},t) \exp\left\{ \frac{U(\mathbf{r})}{2kT} \right\}. \tag{5}$$

With (5), the Smoluchowski equation (4) becomes

$$\frac{\partial}{\partial \tau} \Psi(\mathbf{r};t) = \Delta \Psi(\mathbf{r};t) + \frac{1}{2} \left[\Delta \tilde{U}(\mathbf{r}) - \frac{1}{2} (\nabla \tilde{U}(\mathbf{r}))^2 \right] \Psi(\mathbf{r};t), \tag{6}$$

where $\tau = D_0 t$ and $\tilde{U}(\mathbf{r}) = U(\mathbf{r})/kT$.

With the Green's function known, the molecular mean squared displacements (MSD) can readily be obtained:

$$\langle \mathbf{r}^2(t) \rangle = \frac{1}{Z} \int\int d^3\mathbf{r}_1 d^3\mathbf{r}_0 (\mathbf{r}_1 - \mathbf{r}_0)^2 W(\mathbf{r}_1, \mathbf{r}_0; t) \exp\left\{ -\frac{U(\mathbf{r}_0)}{kT} \right\}, \tag{7}$$

where the statistical integral

$$Z = \int d^3\mathbf{r} \exp\left\{ -U(\mathbf{r})/kT \right\} = V_p \tag{8}$$

is simply equal to the total volume of the pore space. Notably, the Green's function in (7) is the density probability to find a particle at $\mathbf{r}_1$ at the time instance t if at zero time it was located at $\mathbf{r}_0$. The Boltzmann factor in the integral on the right hand side of (7) accounts for the equilibrium distribution of the particles at $t = 0$. The effective diffusivity D_e, which is measured by PFG NMR, is related to the MSDs via (2).

It has earlier been shown [23] that (4) can be solved to yield D_e:

$$D_e(t) = D_0 \left[1 - \frac{D_0}{3t} \left(\frac{1}{kT} \right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \langle \mathbf{f}(t_2)\mathbf{f}(0) \rangle \right], \tag{9}$$

where the force-force autocorrelation function $\langle \mathbf{f}(t)\mathbf{f}(0) \rangle$ is defined as

$$\langle \mathbf{f}(t)\mathbf{f}(0) \rangle = \frac{1}{Z} \int \int d^3\mathbf{r}_1 d^3\mathbf{r}_0 W(\mathbf{r}_1, \mathbf{r}_0; t) \exp\left\{ -\frac{U(\mathbf{r}_0)}{kT} \right\} \frac{\partial}{\partial \mathbf{r}_1} U(\mathbf{r}_1) \frac{\partial}{\partial \mathbf{r}_0} U(\mathbf{r}_0). \tag{10}$$

By substituting $W(\mathbf{r}_1, \mathbf{r}_0; t)$, in analogue with (5), with

$$W(\mathbf{r}_1, \mathbf{r}_0; t) = \exp\left\{ -\frac{U(\mathbf{r}_1)}{2kT} \right\} \Psi(\mathbf{r}_1, \mathbf{r}_0; t), \tag{11}$$

(10) becomes

$$\langle \mathbf{f}(t)\mathbf{f}(0) \rangle = \frac{(2kT)^2}{Z} \int \int d^3\mathbf{r}_1 d^3\mathbf{r}_0 \frac{\partial}{\partial \mathbf{r}_1} \exp\left\{ -\frac{U(\mathbf{r}_1)}{2kT} \right\} \Psi(\mathbf{r}_1, \mathbf{r}_0; t) \frac{\partial}{\partial \mathbf{r}_0} \exp\left\{ -\frac{U(\mathbf{r}_0)}{2kT} \right\}. \tag{12}$$

Notably, $\Psi(\mathbf{r}_1, \mathbf{r}_0; t)$ satisfies (6). The formal solution of the latter equation can be given as

$$\Psi(\mathbf{r}_1, \mathbf{r}_0; t) = \exp\left\{ \tau \hat{L}_1 \right\} \Psi(\mathbf{r}_1, \mathbf{r}_0; 0), \tag{13}$$

where the Liouville operator $\hat{L}_1$ is

$$\hat{L}_1 = \Delta_1 + \frac{1}{2} \left[\Delta_1 \tilde{U}(\mathbf{r}_1) - \frac{1}{2} (\nabla_1 \tilde{U}(\mathbf{r}_1))^2 \right]. \tag{14}$$

The subscript 1 in (14) implies that the differentiation is performed over the position coordinates $\mathbf{r}_1$. By noting that $W(\mathbf{r}_1, \mathbf{r}_0; 0) = \delta(\mathbf{r}_1 - \mathbf{r}_0)$, where $\delta(x)$ is the Dirac delta function, and by using (11), the autocorrelation function $\langle \mathbf{f}(t)\mathbf{f}(0) \rangle$, as given by (12), can finally be given as

$$\langle \mathbf{f}(t)\mathbf{f}(0) \rangle = \frac{(2kT)^2}{Z} \int \int d^3\mathbf{r}_1 d^3\mathbf{r}_0 \left(\frac{\partial}{\partial \mathbf{r}_1} e^{-\frac{U(\mathbf{r}_1)}{2kT}} \frac{\partial}{\partial \mathbf{r}_0} e^{-\frac{U(\mathbf{r}_0)}{2kT}} \right) \exp\left\{ \tau \hat{L}_1 \right\} \delta(\mathbf{r}_1 - \mathbf{r}_0). \tag{15}$$

The major difficulty in evaluating (15) is imposed by the necessity to calculate the function

$$\tilde{W}(\mathbf{r}_1, \mathbf{r}_0; t) \equiv \exp\left\{ \tau \hat{L}_1 \right\} = \exp\left\{ D_0 t \left(\Delta_1 + \frac{1}{2kT} \left[\Delta_1 U(\mathbf{r}_1) - \frac{1}{2kT} (\nabla_1 U(\mathbf{r}_1))^2 \right] \right) \right\}, \tag{16}$$

which cannot be done in the general case.

Let us therefore to consider an approximation, in which we neglect the terms containing the potential energy in the operator $\hat{L}_1$ (14), i.e. assuming that $\hat{L}_1 = \Delta_1$. Under this condition, $\tilde{W}(\mathbf{r}_1, \mathbf{r}_0; t)$ is nothing else than the Green's function for free, unrestricted diffusion, i.e.

$$\tilde{W}(\mathbf{r}_1, \mathbf{r}_0; t) = \exp\left\{ \tau \Delta_1 \right\} = \left(\frac{1}{4\pi D_0 t} \right)^{3/2} \exp\left\{ -\frac{(\mathbf{r}_1 - \mathbf{r}_0)^2}{4 D_0 t} \right\}. \tag{17}$$

The approximation considered turns out to be a reasonable one for the relatively large pore sizes ($R >> a_0$) and for the observation times t satisfying the following condition

$$\tau_R = \frac{R^2}{D_0} \gg t \gg \frac{a_0^2}{D_0} = \tau_0. \tag{18}$$

In (18), τ_0 is a typical time during which the particles diffuse through the surface layer in which they experience a repulsive interaction with pore walls and τ_R is the time to diffuse over distances of the order of the pore sizes. Note that the overall behavior of $\langle \mathbf{f}(t)\mathbf{f}(0)\rangle$ is mainly determined by the ensemble of particles which, at initial times, were residing near the pore walls or within the surface layer a_0. In this respect, the condition 18 ensures that (i) statistics of the particle trajectories between two successive encountering events of the surface layers is described by (17) and (ii) surface orientation between these two points does not change appreciably. With (17), the autocorrelation function simplifies to

$$\langle \mathbf{f}(t)\mathbf{f}(0)\rangle = \\ = \frac{(2kT)^2}{Z}\left(\frac{1}{4\pi D_0 t}\right)^{3/2}\int d^3\mathbf{r}_1 d^3\mathbf{r}_0 \left(\frac{\partial}{\partial \mathbf{r}_1}e^{-\frac{U(\mathbf{r}_1)}{2kT}}\frac{\partial}{\partial \mathbf{r}_0}e^{-\frac{U(\mathbf{r}_0)}{2kT}}\right)\exp\left\{-\frac{(\mathbf{r}_1-\mathbf{r}_0)^2}{4D_0 t}\right\}. \tag{19}$$

Let us now to fix $\mathbf{r}_0$ and to introduce a local coordinate system with $Z(\mathbf{r}_0)$ axis being perpendicular and $X(\mathbf{r}_0)$ and $Y(\mathbf{r}_0)$ axes being parallel to the nearest pore walls, respectively. We may further assume that the potential $U(\mathbf{r})$ varies only along $Z(\mathbf{r}_0)$ direction, but not along $X(\mathbf{r}_0)$ and $Y(\mathbf{r}_0)$. With the condition (18), (19) can be integrated over the coordinates of the position vector $\mathbf{r}_1$ which are parallel to $X(\mathbf{r}_0)$ and $Y(\mathbf{r}_0)$:

$$\langle \mathbf{f}(t)\mathbf{f}(0)\rangle = \\ = \frac{(2kT)^2}{Z}\left(\frac{1}{4\pi D_0 t}\right)^{1/2}\int d\tilde{z}_1 d\tilde{z}_0 d\tilde{x}_0 d\tilde{y}_0 \left(\frac{\partial e^{-\frac{U(\tilde{z}_1)}{2kT}}}{\partial \tilde{z}_1}\frac{\partial e^{-\frac{U(\mathbf{r}_0)}{2kT}}}{\partial \tilde{z}_0}\right)\exp\left\{-\frac{(\tilde{z}_1-\tilde{z}_0)^2}{4D_0 t}\right\}. \tag{20}$$

Note that have introduced a curvilinear coordinate system $\tilde{x}_i(\mathbf{r})_0)$, $\tilde{y}_i(\mathbf{r})_0)$, and $\tilde{z}_i(\mathbf{r})_0)$, which is a function of only the initial position vector $\mathbf{r}_0$, but not $\mathbf{r}_1$ due to (18). Indeed, as it has been discussed in the preceding paragraphs, for the time intervals considered the global surface curvature can be neglected.

The scalar product in the brackets in the integral on the right side hand of (20) is non-zero only within the surface layer close to the pore walls, i.e. when $|\tilde{z}_i(\mathbf{r})_0)| < a_0$, where the gradient of the potential $U(\mathbf{r})$ has a non-zero value. Because $D_0 t >> a_0^2$, we may further use an approximation

$$\exp\left\{-\frac{(\tilde{z}_1-\tilde{z}_0)^2}{4D_0 t}\right\} \approx 1. \tag{21}$$

This allows to integrate (20) over the $\tilde{z}_i$ variables:

$$\int d\tilde{z}_i \frac{\partial}{\partial \tilde{z}_i} e^{-\frac{U(\tilde{z}_i)}{2kT}} = 1. \tag{22}$$

Integration over $\tilde{x}_i(\mathbf{r})_0)$ and $\tilde{y}_i(\mathbf{r})_0)$ yields the total surface area S of the pore walls,

$$\int d\tilde{x}_0(\mathbf{r})_0)d\tilde{y}_0(\mathbf{r})_0) = S. \tag{23}$$

With (8), (22), and (23), $\langle \mathbf{f}(t)\mathbf{f}(0)\rangle$ is obtained as

$$\langle \mathbf{f}(t)\mathbf{f}(0)\rangle = (kT)^2 \frac{S}{V_p}\frac{2}{\sqrt{\pi D_0 t}}. \tag{24}$$

Finally, substituting (24) into (9), results in the short-time effective diffusivity

$$D_e(t) = D_0\left(1 - \frac{8}{9}\frac{S}{V_p}\sqrt{\frac{D_0 t}{\pi}}\right), \tag{25}$$

which is compliant with the previously derived results and differs only by the numerical constant 8/9, as compared to 4/9 in (25).

3. Discussion and conclusions

The diffusivity behavior at short times, as given by (3), was derived in [7] using the Fick's diffusion equation. In this approach, the existence of the impermeable pore walls is accounted for by introducing specific boundary conditions, namely by letting no flux through the pore walls or by equating the gradient of the Green's function in the normal direction to the pore walls to zero, $\partial W(\mathbf{r};t)/\partial r_n{=}0$. In contrast, in this work the existence of the pore walls is considered on a more fundamental level by considering Brownian particles diffusing in a force field generated by the solid matrix, i.e. by applying the Smoluchowski diffusion equation. The penalty is, however, the complexity of the equations arisen, which cannot be solved for arbitrary potential fields. It is therefore certain approximations, e.g. as given by (17), have been considered. Their rigorous justification remains however under discussion.

Irrespective of the approximations used, the result obtained in this study can be considered as a rigorous upper-bond solution for the numerical constant in (25). This can be shown by taking into account the terms in the operator $\hat{L}_1$ (14), which were neglected upon the derivation of (25). Indeed, it turns out that the integral

$$\int_{-\sqrt{D_0 t}}^{\sqrt{D_0 t}} d\tilde{z}_1 \left(\frac{\partial^2 U(z_1)}{\partial z_1^2} - \frac{1}{2kT} \left(\frac{\partial U(z_1)}{\partial z_1} \right)^2 \right) \approx -\frac{1}{2kT} \int_{-\sqrt{D_0 t}}^{\sqrt{D_0 t}} d\tilde{z}_1 \left(\frac{\partial U(z_1)}{\partial z_1} \right)^2 \leq 0 \tag{26}$$

appears to be negative. This means that the Green's function (16) will decay faster as compared to that given by (17). The faster Green's function decay, the higher is the effective diffusivity, implying a lower numerical constant in (25).

In the light of the discrepancy established between the results obtained with the two approaches, (3) and (25), it is instructive to show under which conditions (3) can be obtained using the Smoluchowski equation. Because we are concerned with the time intervals satisfying (18), the Brownian particles can displace by the distances $\sqrt{D_0 t}$ much smaller than the typical curvature R of the pore walls. Hence diffusion parallel to the pore walls can be considered unaltered by the presence of the solid matrix and described by the Green's function for free diffusion. This justifies that the integration over the $\tilde{x}_1(\mathbf{r}_0)$ and $\tilde{y}_1(\mathbf{r}_0)$ variables in (19), i.e. the validity of (20). On the other hand, the times considered are much longer than the typical times $\tau_0 \approx a_0^2/D_0$ the particles spend within the surface layers where their interact with the pore walls. It is therefore the functional form of the Green's function in the direction collinear with $\tilde{z}_1(\mathbf{r}_0)$ can be approached by the Green's function for a half-space convoluted with the equilibrium Boltzmann distribution, i.e.

$$W_z(z_1;t) = \frac{2}{\sqrt{4\pi D_0 t}} \exp\left\{ -\frac{z_1^2}{4D_0 t} \right\} \exp\left\{ -\frac{U(z_1)}{kT} \right\}. \tag{27}$$

With (27) and (10) one can readily obtain (3). In a similar way, (3) has earlier been obtained [24].

The derivation presented in the preceding paragraph poses an important question about which of the approximations used, (17) or (27), can better describe the dynamics of the Brownian particles confined to porous solids. This question can be addressed by either performing diffusion experiments using well-characterized porous materials or by computer simulation studies. In the former case, special care has to be taken to obtain accurately the surface-to-volume ratio of the porous material and to properly account for the surface relaxation effects [8, 25, 26], which can be challenging problems. These difficulties can readily be excluded in computer simulations, e.g. in molecular dynamics studies, in which all relevant parameters can be controlled and the applicability of (17) and (27) can be verified. This work is under progress.

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