On the kinetics of diffusion-controlled processes over long periods of time

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The paper reports an analysis of the effect of sink (trap) diffusion on the phenomenon, observed earlier in the case of stationary sinks [B. Ya. Balagurov and V. G. Vaks, Sov. Phys. JETP **38**, 968 (1974)]; M. D. Donsker and S. R. S. Varadhan, Commun. Pure Appl. Math. **28**, 525 (1975); **32**, 721 (1979); A. A. Ovchinnikov and Ya. B. Zel'dovich, Chem. Phys. **28**, 215 (1978); P. Grassberger and I. Procaccia, J. Chem. Phys. **77**, 6281 (1982)], of fluctuational slowing down of the death of Brownian particles over long periods of time. It is shown that the slowing down of the death also occurs in the case of mobile sinks. In one- and two-dimensional spaces the slowing down occurs at arbitrary sink mobilities, providing the particles are mobile. In the three-dimensional case, for the fluctuational slowing down to occur, it is necessary that the sink diffusion be slow compared to the particle diffusion.

INTRODUCTION

The investigation of the kinetics of a number of physical and physico-chemical processes amounts to the study of the survival of Brownian particles in a medium with randomly distributed mobile sinks (traps), the concentration of which is high compared to the particle concentration. The traditional approach, which derives from Smoluchowski's work,[1] presupposes independent deaths of the particles at each of the sinks. It is exact when the particles are stationary, and the motions of the sinks are uncorrelated. But if the particles are mobile, the probabilities of their deaths at different sinks cease to be independent, and such an approach is inapplicable.

This manifests itself most clearly in the situation in which the sinks are stationary. It is shown in Refs. 2–5 that, in this case, after long periods of time, the deaths occur at a rate lower than the rate predicted by the traditional approach. This is due to the survival of the particles that find themselves in those regions of space which, because of fluctuations, do not contain sinks. The greater the size of such a fluctuation pocket, the longer a particle will survive, since its death outside the pocket will be preceded by a long random walk in a region free of sinks. On the other hand, the bigger the pockets are, the less probable they will be. It is these two circumstances that determine the nature of the so-called fluctuational slowing down.

Thus, the kinetics of the death of particles over long periods of time is clear only in two limiting cases: 1) the case in which the particles are at rest (the traditional approach) and 2) the case in which the sinks are stationary (fluctuational slowing down). The question how these limiting cases go over into each other has not been dealt with in the literature. The purpose of the present paper is to fill this gap.

It is clear that the slower the sink diffusion is, the longer will be the time period over which the diffusion does not play a role, and the particle-death kinetics is the same as in the case of stationary sinks. On the other hand, even very slow sink diffusion, which leads to the swelling of the primordial fluctuation pockets, hastens the death of the particles. This, as we shall see, leads to the replacement of the time dependences obtained in Refs. 2–5 by new dependences, according to which the particle-death rate is higher than in the case of stationary sinks, but lower than the rate predicted by the traditional approach. Thus, the fluctuational slowing down occurs not only in the case of stationary, but also in the case of mobile, sinks.

The time interval over which the sink diffusion does not play a role and the particle-death kinetics is described by the expressions obtained in Refs. 2–5 shortens as the ratio D_s/D_p of the sink- and particle-diffusion coefficients increases. There is no such interval, starting from some characterisic value of this quantity. But even here, in the case of one- and two-dimensional spaces, the particles will, after long periods of time, perish at a rate lower than the rate predicted by the traditional approach, providing they are mobile. In three-dimensional space no slowing down of the death of the particles occurs at such values of the ratio D_s/D_p. This difference in the kinetics is due to the speeding up of the swelling of the sink-free pockets as the dimensionality of the space increases.

Below we shall assume that a particle perishes when it gets within a distance b from a sink, and that the volume fraction of the sinks, which are distributed with density n, is small:

$$nb^d \ll 1, \tag{1}$$

where $d = 1,2,3$ is the dimensionality of the space. Let us represent the probability, of interest to us here, for survival of a particle during a time period t in the form

$$W^{(d)}(t) = \exp[-F^{(d)}(t)]. \tag{2}$$

According to the traditional approach,[6]

$$W^{(d)}(t) = W_{sm}^{(d)}(t) \equiv \exp[-F_{sm}^{(d)}(t)], \tag{3}$$

where at $t \gg b^2/D$

$$F_{sm}^{(3)}(t) \approx 4\pi nbDt, \tag{4}$$

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$$F_{Sm}^{(2)}(t)\approx 4\pi nDt/\ln(Dt/b^2), \quad (5)$$

$$F_{Sm}^{(1)}(t)=4n(Dt/\pi)^{1/2}. \quad (6)$$

Here $D = D_p + D_s$. Next, let us estimate the lower bound for the probability $W^{(d)}(t)$. By comparing this probability with the traditional dependence $W_{Sm}^{(d)}(t)$, we shall find those time intervals over which our estimate yields a higher particle-survival probability. It is precisely there that the fluctuational slowing down occurs. We shall find out how these intervals are related with the ratio D_s/D_p in spaces of different dimensionalities.

THE KINETICS IN THE TWO- AND THREE-DIMENSIONAL CASES

To estimate the probability $W^{(d)}(t)$, we shall use a method similar to the optimal-fluctuation method.[7] Let us introduce a d-dimensional sphere of radius R surrounding a particle at zero time, and let us represent the probability $W^{(d)}(t)$ in the form of a sum of conditional probabilities:

$$W^{(d)}(t)=\sum_{m=0}^{\infty}P_R(m)\,W_R^{(d)}(t,m). \quad (7)$$

Here $W_R^{(d)}(t,m)$ is the probability for survival of the particle over a period of time t under the condition that the sphere contains m sinks at zero time;

$$P_R(m)=(nv_R)^m(m!)^{-1}\exp(-nv_R)$$

is the probability for finding m sinks inside the sphere at $t=0$; and v_R is the volume of the sphere. We can choose the radius R of the sphere at our discretion, requiring only that $R\gg b$.

Since all the terms in (7) are positive,

$$W^{(d)}(t)\geqslant P_R(m=0)\,W_R^{(d)}(t,m=0). \quad (8)$$

Because we are estimating the lower bound for $W^{(d)}(t)$, we have retained in the sum only the term corresponding to the absence of sinks inside the sphere. It can be shown that the slowing down of the death of the particles after long periods of time is due to their survival in precisely the sink-free pockets.

Let us estimate the lower bound for the conditional probability $W_R^{(d)}(t,m=0)$. Since there are no sinks inside the sphere at zero time, the particle will survive over the time period t if all this time is spent inside the sphere and the sphere remains free from sinks during this time. The probability for the particle to remain during a period of time t inside the sphere (of radius R) that surrounds it at zero time is equal to the integral over this sphere's volume of the solution to the d-dimensional diffusion equation

$$\partial c/\partial t=D_p\Delta c$$

with the initial condition $c(\mathbf{r},t=0)=\delta(\mathbf{r})$ and boundary condition $c(|\mathbf{r}|=R,t)=0$. The lower bound of this probability has the form $\exp(-\beta_d D_p t/R^2)$. Here $\beta_3=\pi^2$ and $\beta_2\approx 5.8$ is the square of the first zero of the Bessel function $J_0(z)$. The probability for the preservation during the time period t of a previously-isolated sink-free sphere of radius R is given by the expressions (3)–(5), in which we must replace b by R and set $D=D_s$.

Combining these estimates, we obtain

$$W^{(d)}(t)\geqslant\exp[-F_0^{(d)}(R,t)], \quad (9)$$

where

$$F_0^{(3)}(R,t)\approx\pi^2D_pt/R^2+{}^4/_3\pi nR^3+4\pi nRD_st, \quad (10)$$

$$F_0^{(2)}(R,t)\simeq\beta_2D_pt/R^2+\pi nR^2+4\pi nD_st/\ln(D_st/R^2). \quad (11)$$

In the expressions (10) and (11) the first term determines the probability for a particle to stay inside the sphere of radius R during the time period t; the second term, the probability of finding this sphere free from sinks at zero time; and the last term, the probability of this sphere's remaining free from sinks during the time period t.[1)] Let us emphasize that in the right-hand side of the inequality (9) we have taken the estimate for the lower bound of the conditional probability $W_R^{(d)}(t,m=0)$, ignoring the survival of the particle when it gets out of the pocket, on the other hand, and sinks enter the pocket, on the other.

The subsequent analysis will be carried out according to the following scheme. The radius R of the sphere has thus far been restricted by the single condition: $R\gg b$. Now let us optimize our estimate by choosing $R=R_t$ such that the right-hand side of the inequality (9) has its maximum value at the given moment of time t:

$$(\partial F_0^{(d)}(R,t)/\partial R)_{R=R_t}=0.$$

The value R_t thus found separates out from among the pockets that are free from sinks at zero time $t=0$ the one whose contribution to $W^{(d)}(t)$ at the instant t is maximal. Substituting R_t into (9), we obtain the estimate (of interest to us) for the lower bound of the probability $W^{(d)}(t)$:

$$W^{(d)}(t)\geqslant\exp[-F_0^{(d)}(R_t,t)]\equiv W_0^{(d)}(t). \quad (12)$$

Now let us compare $W_0^{(d)}(t)$ with the traditional dependence $W_{Sm}^{(d)}(t)$. To do this, let us determine the moment of time t_d^* at which $W_0^{(d)}(t)$ and $W_{Sm}^{(d)}(t)$ are equal to each other from the equation

$$F_0^{(d)}(R_{t_d^*},t_d^*)=F_{Sm}^{(d)}(t_d^*). \quad (13)$$

For $t\ll t_d^*$, we have $W_{Sm}^{(d)}\gg W_0^{(d)}(t)$, and the survival of the particles in the sink-free pockets does not play a special role. Here the probability for survival is given by the traditional expression $W^{(d)}(t)\approx W_{Sm}^{(d)}(t)$, and the fluctuational slowing down does not occur. The fluctuational slowing down occurs in the region $t\gg t_d^*$, where $W_{Sm}^{(d)}(t)\ll W_0^{(d)}(t)$, and the kinetics is governed precisely by the survival of the particles in the sink-free pocket: $W^{(d)}(t)\approx W_0^{(d)}(t)$.

Let us note that, at times when the fluctuational slowing down does occur, the neglect of the survival of the particles that have left a pocket is justified, since the radius R_t is large compared with the characteristic distance over which a particle perishes outside a pocket. Also justified is the neglect of the survival of the particles in a pocket containing at least one sink, since the characteristic particle-survival time in such a pocket is short compared to t. For the corresponding estimate we can use the traditional expressions (3)–(5) with $n=1/v_{R_t}$.

Let us proceed to the description of the dependences obtained as a result of the analysis presented above. In the three-dimensional case the fluctuational slowing down occurs only when the mobility of the sinks is low:

$$D_s/D_p \ll (nb^3)^{1/2} \ll 1. \tag{14}$$

In the opposite case, when $D_s/D_p \gg (nb^3)^{1/2}$, Eq. (13) does not possess solutions, and at all times the particle-survival probability is given by the traditional expression $W^{(3)}(t) \approx W_{Sm}^{(3)}(t)$.

For the description of the resulting picture, it is convenient to introduce the dimensionless time

$$\tau = 4\pi nbDt,$$

choosing as the scale the particle lifetime in the traditional dependence (see (3) and (4)), which in this case has the form

$$W_{Sm}^{(3)}(\tau) \approx e^{-\tau}. \tag{15}$$

When the condition (14) is fulfilled, the solution of Eq. (13) yields

$$\tau_3^* = 4\pi nbDt_3^* \approx 4\pi (nb^3)^{-1/2}.$$

The nature of the fluctuational slowing down phenomenon varies in time. In the time interval defined by the inequality

$$\tau_3^* \ll \tau \ll 4\pi (D_p/D_s)^{5/3} (nb^3)^{1/3}, \tag{16}$$

the diffusion of the sinks is of no importance, and the particle-death kinetics is governed by the well-known expression obtained in Refs. 2–5. Here

$$R_t \approx n^{-1/3} [D_p \tau / 8D (nb^3)^{1/3}]^{1/5},$$
$$W^{(3)}(\tau) \approx W_0^{(3)}(\tau) \approx \exp[-(5\pi/2^{4/5}\cdot 3)\tau^{3/5}/(nb^3)^{1/5}]. \tag{17}$$

The fact that we can neglect the swelling of the sink-free pockets in the time interval defined by the inequality (16) follows from a comparison of the terms in the expression $F_0^{(3)}$ (see (10)). This swelling should be taken into account at large τ values, specifically, at

$$\tau \gg 4\pi (D_p/D_s)^{5/3} (nb^3)^{1/3}. \tag{18}$$

The point is that the probability for a pocket's remaining free from sinks during the time period t decreases as the radius of the pocket increases (see (10)). Therefore, the growth of the radius R_t in time ceases, and at times satisfying the condition (18) $R_t \approx n^{-1/3} (\pi D_p / 2D_s)^{1/3}$. As a result here

$$W^{(3)}(\tau) \approx W_0^{(3)}(\tau) \approx \exp[-(3\pi^{1/3}/2^{4/3}) (D_p/D_s)^{2/3} \tau/(nb^3)^{1/3}]. \tag{19}$$

Let us emphasize that, although the index of the exponential function in (19) is linear in τ, just as obtains in the traditional dependence (15), the expression (19) gives a particle-death rate lower by a factor of the order of $(D_p/D_s)^{2/3}(nb^3)^{-1/3}$ (see (14)) than the rate predicted by the traditional approach. For $D_s \to 0$, the instant when the sink diffusion begins to play a role shifts, in accordance with (18), to infinity. Figure 1 shows a schematic drawing of the regions of applicability of the various approximations to the probability $W^{(3)}(\tau)$.

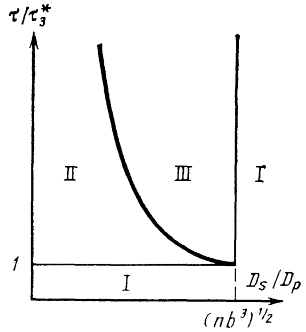

FIG. 1. Diagram of the regions of applicability of the various approximations to the probability $W^{(3)}(\tau)$ for particle survival in three-dimensional space. In the region I the traditional approach is applicable, and $W^{(3)}(\tau)$ is given by the expression (15). The fluctuational slowing down occurs in the regions II and III. In the region II the neglect of the sink diffusion is justified, and $W^{(3)}(\tau)$ is given by the expression (17). In the region III the sink diffusion plays an important role, and $W^{(3)}(\tau)$ is given by the expression (19). The line $\tau = 4\pi(nb^3)^{1/3}(D_p/D_s)^{5/3}$ separates the regions II and III.

In the two-dimensional case, as the dimensionless time, it is convenient to take (see (3) and (5))

$$\tau = 4\pi nDt.$$

In this case the traditional dependence has the form

$$W_{Sm}^{(2)}(\tau) \approx \exp[-\tau/\ln(\tau/4\pi nb^2)]. \tag{20}$$

When the sinks are of low mobility, i.e., for

$$D_s/D_p \ll 1/\ln(1/nb^2) \ll 1, \tag{21}$$

the solution of Eq. (13) yields

$$\tau_2^* = 4\pi nDt_2^* \approx \beta_2 \ln^2(\beta_2/\pi nb^2). \tag{22}$$

In the time interval defined by the inequalities

$$\tau_2^* \ll \tau \ll 4\pi (D_p/D_s)^2, \tag{23}$$

the diffusion of the sinks has no effect on the kinetics that is characteristic of the fluctuational slowing down phenomenon in the case of stationary sinks.[1,3,5] Here

$$R_t \approx n^{-1/2} (\beta_2 D_p \tau / 4\pi^2 D_s)^{1/4},$$
$$W^{(2)}(\tau) \approx W_0^{(2)}(\tau) \approx \exp(-\beta_2^{1/2}\tau^{1/2}). \tag{24}$$

At large τ values, specifically, at

$$\tau \gg 4\pi (D_p/D_s)^2, \tag{25}$$

the nature of the fluctuational slowing down phenomenon changes, since the diffusion-induced swelling of the sink-free pockets play an important role. Since it occurs more slowly in two-dimensional space than in three-dimensional space, it only slows down the growth of the radius R_t in time: the dependence $R_t \propto \tau^{1/4}$ is replaced by

$$R_t \approx \left(\frac{\beta_2}{4\pi}\frac{D_p}{nD_s}\right)^{1/2} \ln\left(\frac{D_s^2\tau}{\beta_2 D_p D}\right).$$

Here this swelling controls the kinetics, and

$$W^{(2)}(\tau) \approx W_0^{(2)}(\tau) \approx \exp\left[-\frac{4\pi nD_s t}{\ln(D_s t/R_t^2)}\right]$$
$$\approx \exp\left(-\frac{D_s}{D}\frac{\tau}{\ln\tau}\right) \tag{26}$$

(cf. the last term in (11)). According to (26), the particles perish at a rate lower (to the extent that the ratio D_s/D is small) than the rate predicted by the traditional dependence.

A consequence of the above-noted slowness of the swelling of the fluctuational pockets in the two-dimensional case as compared with the three-dimensional case is that here the fluctuational slowing down occurs at any value of the ratio D_s/D_p. The expression (26) is valid not just when the mobility of the sinks is low and the condition (21) is fulfilled, but for arbitrary sink mobility. If the opposite of the inequality (21), i.e., the inequality

$$D_s/D_p \gg \frac{1}{\ln(1/nb^2)}, \tag{27}$$

is valid, then the well-known kinetics (24) corresponding to the case of stationary sinks is not realized at all. In this case the region of applicability of the dependence (26) is specified by the condition $\tau \gg \tau_2^*$, and the time τ_2^* is equal to

$$\tau_2^* = 4\pi \frac{D_p D}{D_s^2} (\Gamma \ln \Gamma)^{2D/D_p}, \qquad \Gamma = \frac{2D}{D_p}\left(\frac{\beta_2}{4\pi}\frac{D_p D}{nb^2 D_s^2}\right)^{D_s/2D} \tag{28}$$

Thus, in the case of two-dimensional space, in contrast to the case of three-dimensional space, the fluctuational slowing down occurs at any value of the sink mobility, providing the particles are mobile. According to (25) and (28), in both the $D_s \to 0$ and $D_p \to 0$ cases, the limits of the region of applicability of the dependence (26) tend to infinity. Figure 2 shows a schematic drawing of the regions of applicability of the various approximations to $W^{(2)}(\tau)$.

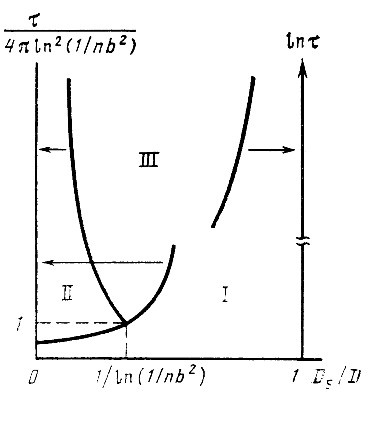

FIG. 2. Diagram of the regions of applicability of the various approximations to the probability $W^{(2)}(\tau)$ for particle survival in two-dimensional space. In the region I the traditional approach is applicable, and $W^{(2)}(\tau)$ is given by the expression (20). The fluctuational slowing down occurs in the regions II and III. In the region II the neglect of the sink diffusion is justified, and $W^{(2)}(\tau)$ is given by the expression (24). In the region III the diffusion induced swelling of the sink-free pockets governs the kinetics, and $W^{(2)}(\tau)$ is given by the expression (26). The regions II and III are separated by the line $\tau = 4\pi(D/D_s)$.[2] The regions I and III for $D_s/D > \ln^{-1}(1/nb^2)$ are separated by the line $\tau = \tau_2^*$, where τ_2^* is given by the expression (28).

THE KINETICS IN THE ONE-DIMENSIONAL CASE

Let us use the fact that, in one-dimensional space, the problem of the survival of a mobile particle in a stationary-sink environment has an exact solution[2]:

$$\overline{W}(t, D_p) = \frac{4}{\pi^2}\int_0^\infty \exp\left(-\frac{\pi^2 n^2 D_p t}{x^2}\right)\frac{x\,dx}{\operatorname{sh} x}. \tag{29}$$

We shall represent the estimate of interest to us in the form of a product of the probability $\overline{W}(t,D_p)$ and the probability for the preservation over the time period t of the sink-free regions surrounding the particles at zero time. The latter probability is given by the expressions (3) and (6) with $D = D_s$. As a result, we obtain

$$W^{(1)}(t) \geqslant W_0^{(1)}(t) = \overline{W}(t, D_p)\exp\left[-\frac{4n}{\pi^{1/2}}(D_s t)^{1/2}\right]. \tag{30}$$

The right-hand side of (30) gives the lower bound, since it ignores the change that occurs in the lifetime of the particles as a result of the change in the sink-free regions surrounding them at zero time. In both the $D_p = 0$, $D_s \neq 0$ and $D_s = 0$, $D_p \neq 0$ cases, the right-hand side of (30) coincides with the corresponding exact solutions. For $D_p \neq 0$ and $D_s \neq 0$, it can be considered to be an interpolation formula.

Equating the estimate (30) to the traditional expression for the probability, i.e., for $W_{Sm}^{(1)}(t)$ (see (3), (6)), we find the moment of time t_1^* starting from which fluctuational slowing down occurs. It is again convenient to introduce the dimensionless time (see (3), (6))

$$\tau = 16\pi^{-1}n^2 Dt.$$

The traditional dependence then has the form

$$W_{Sm}^{(1)}(\tau) = \exp(-\tau^{1/2}). \tag{31}$$

The time $\tau_1^* = 16n^2Dt_1^*/\pi$ is equal to[2)]

$$\tau_1^* = \left(\frac{3\pi}{4}\right)^6 \frac{[1+(D_s/D)^{1/2}]^2}{[1-(D_s/D)^{1/2}]^4}. \tag{32}$$

In the region $\tau \gg \tau_1^*$ there occurs fluctuational slowing down, and the particle-survival probability is given by the expression

$$W^{(1)}(\tau) \approx W_0^{(1)}(\tau) \approx \exp\left\{-\left[\frac{3\pi}{4}\left(\frac{D_p}{D}\right)^{1/3}\tau^{1/3} + \left(\frac{D_s}{D}\right)^{1/2}\tau^{1/2}\right]\right\}. \tag{33}$$

For $D_s/D < \frac{1}{4}$, the picture that obtains in the time interval specified by the inequality

$$\tau_1^* \ll \tau \ll (3\pi/4)^6 D_p^2 D/D_s^3, \tag{34}$$

in the case of stationary sinks is not altered by the diffusion of the sinks. Here the first term in the index of the exponential function (33) predominates, and the particle-survival probability is given by the well-known expression obtained in Refs. 2, 3, and 5. At large τ values, specifically, at

$$\tau \gg (3\pi/4)^6 D_p^2 D/D_s^2, \tag{33}$$

the diffusion of the sinks accelerates the death of the particles in comparison with the $D_s = 0$ case. Here the dominant term in the index of the exponential function (33) is the second term, which gives the probability for the preservation of the fluctuational regions in the time interval t. The resulting kinetics describes a slower (to the extent that the ratio

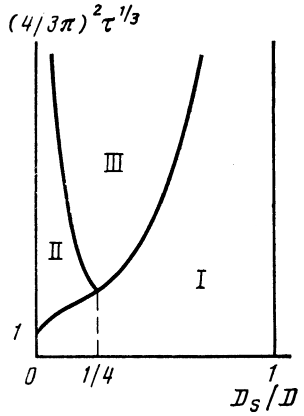

FIG. 3. Diagram of the regions of applicability of the various approximations to the probability $W^{(1)}(\tau)$ for particle survival in one-dimensional space. In the region I the traditional approach is applicable, and $W^{(1)}(\tau)$ is given by the expression (31). The fluctuational slowing down occurs in the regions II and III, in which the survival probability $W^{(1)}(\tau)$ is given by the expression (33). In the region II the neglect of the sink diffusion is justified: the first term in the index of the exponential function (33) is the dominant term. In the region III the diffusion-induced swelling of the sink-free pockets governs the kinetics: the second term in the index of the exponential function (33) is the dominant term. The regions II and III are separated by the line $\tau = (3\pi/4)^6 D_p^2 D/D_s^3$. The region I is separated from the regions II and III by the line $\tau = \tau_1^*$, where τ_1^* is given by the expression (32).

D_s/D is small) particle death rate than the traditional dependence (31).

This kinetics is valid after long periods of time at any value of D_s/D. For $D_s/D > \frac{1}{4}$ the well-known dependences obtained in Refs. 2, 3, and 5 for stationary sinks are not realized at all, and at times $\tau \gg \tau_1^*$ there immediately arises kinetics governed by the diffusion-induced swelling of the fluctuation regions. In both the $D_p \to 0$ and $D_s \to 0$ cases the limits of the regions of applicability of this kinetics tend, in accordance with (33) and (35), to infinity. Thus, in the one-dimensional case (as in the two-dimensional, but unlike the three-dimensional, case), the particle-death rate after long periods of time is lower at any value of the ratio D_s/D than the rate obtained in the traditional approach. Figure 3 shows a diagram of the regions of applicability of the various approximations to $W^{(1)}(\tau)$.

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[1)]The expressions used for the probability for the pockets of radius R to remain sink free during the period of time t are valid for $t \gg R^2/D_s$. The estimates obtained below for $W^{(d)}(t)$ satisfy this condition.

[2)]Since $t_1^* \gg 1/\pi^2 n^2 D_p$, to find t_1^*, we used the asymptotic form of $\overline{W}(t, D_p)$ for large t.

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