Diffusion and absorption in a medium with spherical sinks[a)]

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We consider particles diffusing in a uniform medium and being absorbed by statistically distributed spherical sinks. We study the average diffusion–absorption equation, as derived to first order in the sink density by multiple-scattering theory. We show that for perfect sinks this equation must be modified to take proper account of instantaneous absorption of particles created inside the sinks.

I. INTRODUCTION

In the theory of diffusion-controlled reactions one considers particles diffusing in a medium and being absorbed by randomly distributed sinks. If the sink system is sufficiently dilute, the average absorption rate is proportional to the sink density and the rate coefficient can be calculated from the properties of a single sink. In this calculation, first performed by Smoluchowski,[1] one considers the steady rate of absorption by the sink when particles are supplied uniformly at infinity. Smoluchowski also considered the initial-value problem, and displayed the long-time effects that are present in time-dependent situations. In earlier articles we studied higher order density corrections to the rate coefficient in the steady state,[2] as well as in the time-dependent case.[3] We pointed out[2] that in the average diffusion–absorption equation the diffusion coefficient is also modified by the presence of sinks. To first order in the sink density one can perform a calculation similar to Smoluchowski's and consider a single sink placed in a uniform gradient of particle density.

Our work[2,3] was based on a local field method. The density field acting on any chosen sink satisfies the free field equation in the absence of the sink. One then uses a hierarchy of conditionally averaged equations to establish the average response of the sink. The method precludes the possibility that particles are created inside the sinks. Alternatively, one may use the formalism of multiple scattering theory,[4-6] in which case the source density may overlap with the sinks. To linear order in the sink density this theory is a direct generalization of work by Foldy[7] and by Lax.[8]

In this article we point out a difficulty with the straightforward application of the Foldy–Lax scheme which is highlighted for the case of perfect sinks. Particles produced inside a perfect sink are absorbed instantaneously. We argue that the average diffusion–absorption equation must be modified in such a way that the effects of instantaneous absorption are clearly identifiable.

We derive the average equation and its proposed modification in Secs. II–V. In Sec. VI we apply a multipole expansion to both equations and hence derive macroscopic equations by retaining only terms to second order in the spatial gradients. In Sec. VII we discuss the modified macroscopic equation and in Sec. VIII we compare our results with the recent results of Bixon and Zwanzig.[5]

II. ABSORBING SINK

We first consider the problem of pointlike particles diffusing in a uniform medium and being absorbed by a single spherical sink. The diffusion–absorption equation for the particle number density $c(\mathbf{r}, t)$ in the presence of a single sink centered at the origin reads

$$\frac{\partial c}{\partial t} = D_0 \nabla^2 c - \lambda(r) c + s(\mathbf{r}, t) , \tag{2.1}$$

where D_0 is the diffusion coefficient, $\lambda(r)$ is the local absorption coefficient, and $s(\mathbf{r}, t)$ is the source density. For simplicity we assume the local absorption coefficient to be given by

$$\begin{aligned} \lambda(r) &= \lambda , \quad \text{for} \quad |\mathbf{r}| < a , \\ &= 0 , \quad \text{for} \quad |\mathbf{r}| > a , \end{aligned} \tag{2.2}$$

where a is the radius of the sink. More complicated models can be envisaged. The source density $s(\mathbf{r}, t)$ supplies new particles to the system and is a given function of space and time. To familiarize the reader with the problem we consider some simple situations.

In case there is a constant and isotropic source at infinity, the stationary solution of Eq. (2.1) reads

$$\begin{aligned} c(r) &= c_\infty A \frac{\sinh \nu r}{r} , \quad r < a , \\ &= c_\infty \left(1 - \frac{B}{r}\right) , \quad r > a , \end{aligned} \tag{2.3}$$

where $\nu = \sqrt{\lambda / D_0}$. The coefficients A and B follow from continuity of $c(r)$ and $c'(r)$ at $r = a$. One finds

$$A = (\nu \cosh \nu a)^{-1} , \quad B = a\left(1 - \frac{\tanh \nu a}{\nu a}\right) . \tag{2.4}$$

The total absorption rate for the sphere is given by

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$$J=\int \lambda(r)c(r)d\mathbf{r}=4\pi D_0 B c_\infty \ , \tag{2.5}$$

corresponding to the rate coefficient

$$k=4\pi D_0 B \ . \tag{2.6}$$

In the limit $\lambda \to \infty$ the sink becomes perfectly absorbing and the rate approaches $J=4\pi D_0 a c_\infty$ with the Smoluchowski rate coefficient $k_s=4\pi D_0 a$.

In case there is a constant and uniform source inside the sink, i.e., the source density is given by $s(\mathbf{r})=s\theta(a-r)$, where $\theta(a-r)$ is the step function, the stationary solution of Eq. (2.1) reads

$$\begin{aligned} c(r) &= \frac{s}{\lambda}\left(1-A\frac{\sinh \nu r}{r}\right), \quad r<a \ , \\ &= \frac{s}{\lambda}\frac{B}{r} , \qquad r>a \ , \end{aligned} \tag{2.7}$$

with coefficients A and B again given by Eqs. (2.4). Clearly, the particles can diffuse outwards and some finally escape to infinity. The escape rate is given by

$$E=4\pi D_0 B\frac{s}{\lambda} \ . \tag{2.8}$$

Hence, the rate of absorption by the sink is

$$J'=S-E \ , \tag{2.9}$$

where $S=(4\pi/3)a^3 s$ is the total source strength. The probability of escape is

$$p_e=E/S=3D_0B/\lambda a^3 \ . \tag{2.10}$$

Expressing Eq. (2.10) in terms of the rate coefficient $k=4\pi D_0 B$, one finds

$$p_e=\frac{3}{4\pi a^3}\frac{k}{\lambda} \ . \tag{2.11}$$

From Eqs. (2.4) one finds

$$p_e=\frac{3}{\nu^2 a^2}\left(1-\frac{\tanh \nu a}{\nu a}\right) , \tag{2.12}$$

which exhibits the limiting behavior $p_e \to 0$ for $D_0 \to 0$, and $p_e \to 1$ for $D_0 \to \infty$ at fixed λ.

The above examples demonstrate that it is of interest to distinguish between particles created inside the sink and those created outside. We may visualize these particles as colored red and blue, respectively, and we can follow their separate fates.

More generally, we shall consider time-dependent situations. It is then convenient to take Fourier transforms and to write

$$s(\mathbf{r},t)=\int s_\omega(\mathbf{r})\,e^{-i\omega t}d\omega \ , \tag{2.13}$$

and similarly for $c(\mathbf{r},t)$. We define the local absorption rate $a(\mathbf{r},t)$ by

$$a(\mathbf{r},t)=\lambda(r)c(\mathbf{r},t) \ . \tag{2.14}$$

Since our basic equation (2.1) is linear and time-translation invariant, the local absorption is related by a linear operator $Y(\mathbf{r},\mathbf{r}',\omega)$ to the source density according to

$$a_\omega(\mathbf{r})=\int Y(\mathbf{r},\mathbf{r}',\omega)s_\omega(\mathbf{r}')d\mathbf{r}' \ . \tag{2.15}$$

We can distinguish between particles created inside and outside the sink by writing

$$Y(\omega)=Y_{\text{in}}(\omega)+Y_{\text{ou}}(\omega) \ , \tag{2.16}$$

with

$$\begin{aligned} Y_{\text{in}}(\mathbf{r},\mathbf{r}',\omega)&=\lambda(r)G_s(\mathbf{r},\mathbf{r}',\omega)\theta(a-r') \ , \\ Y_{\text{ou}}(\mathbf{r},\mathbf{r}',\omega)&=\lambda(r)G_s(\mathbf{r},\mathbf{r}',\omega)\theta(r'-a) \ , \end{aligned} \tag{2.17}$$

where $G_s(\mathbf{r},\mathbf{r}',\omega)$ is the Green function in the presence of the sink.

The operator $Y(\omega)$ is closely related to the T matrix for the problem. If the sink were absent, the diffusion equation would read

$$\frac{\partial c^{\text{ex}}}{\partial t}=D_0\nabla^2 c^{\text{ex}}+s(\mathbf{r},t) \ . \tag{2.18}$$

Fourier transforming Eqs. (2.1) and (2.18), one finds

$$-i\omega c_\omega(\mathbf{r})=D_0\nabla^2 c_\omega(\mathbf{r})-\lambda(r)c_\omega(\mathbf{r})+s_\omega(\mathbf{r}) \ , \tag{2.19a}$$

$$-i\omega c_\omega^{\text{ex}}(\mathbf{r})=D_0\nabla^2 c_\omega^{\text{ex}}(\mathbf{r})+s_\omega(\mathbf{r}) \ . \tag{2.19b}$$

The effect of the sink is expressed by the T matrix $T(\mathbf{r},\mathbf{r}',\omega)$ defined by

$$a_\omega(\mathbf{r})=\lambda(r)c_\omega(\mathbf{r})=\int T(\mathbf{r},\mathbf{r}',\omega)c_\omega^{\text{ex}}(\mathbf{r}')d\mathbf{r}' \ . \tag{2.20}$$

A comparison with Eq. (2.15) shows that $Y(\omega)$ and $T(\omega)$ are related by

$$Y(\omega)=T(\omega)G_0(\omega) \ , \tag{2.21}$$

where $G_0(\omega)$ is the Green function for Eq. (2.19b). Explicitly,

$$G_0(\mathbf{r},\mathbf{r}',\omega)=\frac{1}{4\pi D_0}\frac{\exp(-\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} , \tag{2.22}$$

where $\mu=\sqrt{-i\omega/D_0}$. Clearly, this is a symmetric kernel. One can show that the T matrix $T(\mathbf{r},\mathbf{r}',\omega)$ is also symmetric. The decomposition (2.16) leads to a corresponding decomposition of the T matrix. In plane wave representation

$$\begin{aligned} \langle\mathbf{k}|T_{\text{in}}(\omega)|\mathbf{k}'\rangle &\equiv \int \exp(-i\mathbf{k}\cdot\mathbf{r})T_{\text{in}}(\mathbf{r},\mathbf{r}',\omega)\exp(i\mathbf{k}'\cdot\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' \\ &= \langle\mathbf{k}|Y_{\text{in}}(\omega)|\mathbf{k}'\rangle(-i\omega+D_0k'^2) \ , \end{aligned} \tag{2.23}$$

with a corresponding expression for $T_{\text{ou}}(\omega)$.

III. MANY SINKS

We now consider particles diffusing and being absorbed by a system of many identical sinks. The diffusion–absorption equation for the particle density reads

$$\frac{\partial c}{\partial t}=D_0\nabla^2 c-\lambda(1,\ldots,N)c+s(\mathbf{r},t) \ , \tag{3.1a}$$

where $\lambda(1,\ldots,N)\equiv\lambda(\mathbf{R}_1,\ldots,\mathbf{R}_N)$ is the local absorption coefficient given by

$$\begin{aligned} \lambda(\mathbf{r};\mathbf{R}_1,\ldots,\mathbf{R}_N)&=\lambda, \quad \text{if } |\mathbf{r}-\mathbf{R}_j|\leqslant a \text{ for some } j \ , \\ &=0, \quad \text{if } |\mathbf{r}-\mathbf{R}_j|>a \text{ for all } j \ , \end{aligned} \tag{3.1b}$$

where $\mathbf{R}_j$ is a sink center. We assume that the sinks do not overlap and are statistically distributed, as described by a given probability distribution $P(\mathbf{R}_1, \ldots, \mathbf{R}_N)$. In some physical situations of interest the source density $s(\mathbf{r}, t)$ will be correlated with the sink positions, but we shall first consider the simpler uncorrelated case.

To find the average diffusion and absorption of particles in the many-sink system, we average Eq. (3.1a) over the probability distribution $P(\mathbf{R}_1, \ldots, \mathbf{R}_N)$. Results to arbitrary order in the density of sinks may be obtained by use of the cluster expansion formalism developed recently by Felderhof, Ford, and Cohen.[9] Here we merely aim at obtaining the transport coefficients correctly to first order in the sink density. We begin by recalling the method developed, to this order, by Foldy[7] and Lax[8] in the theory of multiple scattering.

The Fourier transform of Eq. (3.1a) reads

$$-i\omega c_\omega(\mathbf{r}) = D_0\nabla^2 c_\omega(\mathbf{r}) - \lambda(1, \ldots, N)c_\omega(\mathbf{r}) + s_\omega(\mathbf{r}). \qquad (3.2)$$

We define the N-body absorption rate by

$$a(\mathbf{r}, t; 1, \ldots, N) = \lambda(\mathbf{r}; 1, \ldots, N)c(\mathbf{r}, t) \ . \qquad (3.3)$$

The effect of the sinks is conveniently described with the aid of the N-body T matrix defined by

$$a_\omega(\mathbf{r}; 1, \ldots, N) = \int T(\mathbf{r}, \mathbf{r}', \omega; 1, \ldots, N)c_\omega^{\rm ex}(\mathbf{r}')d\mathbf{r}' \ . \qquad (3.4)$$

In shorthand operator notation

$$a_\omega(1, \ldots, N) = T(\omega; 1, \ldots, N)c_\omega^{\rm ex} \ . \qquad (3.5)$$

The solution of Eq. (3.2) can be written

$$c_\omega(1, \ldots, N) = G_0(\omega)[-a_\omega(1, \ldots, N) + s_\omega] \ . \qquad (3.6)$$

Using $c_\omega^{\rm ex} = G_0(\omega)s_\omega$ and substituting Eq. (3.5), we obtain

$$c_\omega(1, \ldots, N) = [I - G_0(\omega)T(\omega; 1, \ldots, N)]c_\omega^{\rm ex} \ . \qquad (3.7)$$

Equations (3.2), (3.5), and (3.7) can now be averaged over the probability distribution $P(\mathbf{R}_1, \ldots, \mathbf{R}_N)$. Defining the averages

$$C_\omega(\mathbf{r}) = \langle c_\omega(\mathbf{r})\rangle \ , \quad A_\omega(\mathbf{r}) = \langle a_\omega(\mathbf{r})\rangle \ , \qquad (3.8)$$

we find from Eq. (3.2)

$$-i\omega C_\omega(\mathbf{r}) = D_0\nabla^2 C_\omega(\mathbf{r}) - A_\omega(\mathbf{r}) + s_\omega(\mathbf{r}) \ . \qquad (3.9)$$

To lowest order in the density the N-body T matrix can be replaced by a sum of one-body T matrices

$$T(\omega; 1, \ldots, N) \approx \sum_{j=1}^{N} T(\omega; j) \ . \qquad (3.10)$$

Averaging Eq. (3.5) with this approximation, one finds

$$A_\omega(\mathbf{r}) = \int n(\mathbf{R}_1)T(\mathbf{r}, \mathbf{r}', \omega; \mathbf{R}_1)c_\omega^{\rm ex}(\mathbf{r}')d\mathbf{r}'\, d\mathbf{R}_1 \ , \qquad (3.11)$$

where $n(\mathbf{R}_1)$ is the one-particle density. Similarly, by averaging Eq. (3.7),

$$C_\omega(\mathbf{r}) = c_\omega^{\rm ex}(\mathbf{r}) - \int n(\mathbf{R}_1)G_0(\mathbf{r}, \mathbf{r}', \omega) \times T(\mathbf{r}', \mathbf{r}'', \omega; \mathbf{R}_1)c_\omega^{\rm ex}(\mathbf{r}'')d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{R}_1 \ . \qquad (3.12)$$

To lowest order in the sink density $C_\omega = c_\omega^{\rm ex}$ so that, to first order in the density, Eq. (3.11) yields the constitutive equation

$$A_\omega(\mathbf{r}) = \int n(\mathbf{R}_1)T(\mathbf{r}, \mathbf{r}', \omega; \mathbf{R}_1)C_\omega(\mathbf{r}')d\mathbf{r}'\, d\mathbf{R}_1 \qquad (3.13)$$

or in shorthand notation

$$A_\omega = K(\omega)C_\omega \ , \qquad (3.14)$$

where

$$K(\omega) = \int n(\mathbf{R}_1)T(\omega; \mathbf{R}_1)d\mathbf{R}_1 \ . \qquad (3.15)$$

Substituting Eq. (3.14) in Eq. (3.9), one finds the low density average equation

$$-i\omega C_\omega(\mathbf{r}) = D_0\nabla^2 C_\omega(\mathbf{r}) - \int K(\mathbf{r}, \mathbf{r}', \omega)C_\omega(\mathbf{r}')d\mathbf{r}' + s_\omega(\mathbf{r}) \ . \qquad (3.16)$$

The one-body T matrix $T(\mathbf{r}, \mathbf{r}', \omega; \mathbf{R}_1) = T(\mathbf{r} - \mathbf{R}_1, \mathbf{r}' - \mathbf{R}_1, \omega)$ is symmetric in $\mathbf{r} - \mathbf{R}_1$ and $\mathbf{r}' - \mathbf{R}_1$ and vanishes identically for $|\mathbf{r} - \mathbf{R}_1| > a$, $|\mathbf{r}' - \mathbf{R}_1| > a$. Hence, it follows that the absorption kernel $K(\mathbf{r}, \mathbf{r}', \omega)$ vanishes for $|\mathbf{r} - \mathbf{r}'| > 2a$.

If the density of sinks $n(\mathbf{R}_1)$ is spatially uniform, then K becomes a translationally invariant kernel $K(\mathbf{r} - \mathbf{r}', \omega)$. Defining the Fourier transform

$$C_{\mathbf{k},\omega} = \frac{1}{8\pi^3}\int C_\omega(\mathbf{r}) \exp(-i\mathbf{k}\cdot \mathbf{r})d\mathbf{r} \ , \qquad (3.17)$$

one finds from Eq. (3.16)

$$-i\omega C_{\mathbf{k},\omega} = -D_0k^2 C_{\mathbf{k},\omega} - nt(\mathbf{k}, \mathbf{k}, \omega)C_{\mathbf{k},\omega} + s_{\mathbf{k},\omega} \ , \qquad (3.18)$$

where

$$t(\mathbf{k}, \mathbf{k}, \omega) \equiv \langle \mathbf{k}|T(\omega)|\mathbf{k}\rangle = \int \exp(-i\mathbf{k}\cdot \mathbf{r})T(\mathbf{r}, \mathbf{r}', \omega) \exp(i\mathbf{k}\cdot \mathbf{r}')d\mathbf{r}\, d\mathbf{r}' \qquad (3.19)$$

is the **kk** element of the T matrix for a sphere centered at the origin. Equation (3.18) has the form derived by Foldy and Lax. Solving Eq. (3.18), one finds the Green function

$$G(\mathbf{k}, \omega) = [-i\omega + D_0k^2 + nt(\mathbf{k}, \mathbf{k}, \omega)]^{-1} \ . \qquad (3.20)$$

Equation (3.16) and its associated Green function can be regarded as the generalization of Eqs. (3.18) and (3.20) to spatially varying sink density.

As stated at the beginning of this section, we have assumed in our derivation that the source density $s(\mathbf{r}, t)$ is not correlated with the sink positions. If we confront a problem where the particle creation occurs inside a sink, or is otherwise correlated with the sink position, then we must modify the formalism. The change required is that we take conditional averages with the position of the selected sink held fixed. After deriving the conditionally averaged equation, this equation may be solved and a final average of the solution over the selected variable may be carried out. In this manner we can, for example, distinguish between particles created inside and outside the sinks. Also, one could study how the probability of escape p_e is affected by surrounding sinks. We shall leave the treatment of such problems to a following article and restrict ourselves here to the study of the special limiting case of perfectly absorbing sinks. In this case any particles created inside a sink are instantaneously absorbed, so that the average concentration $C(\mathbf{r}, t)$ pertains only to particles created outside the sinks. It then suffices to study the average equation for $C(\mathbf{r}, t)$.

IV. PERFECT SINK

We first consider a single perfectly absorbing sink, corresponding to the limit $\lambda \to \infty$. For this case we give here explicit expressions for some of the quantities introduced in Sec. II. The diffusion–absorption equation for a single sink centered at the origin can be written

$$-i\omega c_\omega(\mathbf{r}) = D_0 \nabla^2 c_\omega(\mathbf{r}) - a_\omega(\mathbf{r}) + s_\omega(\mathbf{r}) \ , \tag{4.1}$$

with the condition

$$c_\omega(\mathbf{r}) = 0 \ , \quad \text{for } r < a \ . \tag{4.2}$$

The absorption rate $a_\omega(\mathbf{r})$ is given by

$$a_\omega(\mathbf{r}) = s_\omega(\mathbf{r})\theta(a-r) + \sigma_\omega(\mathbf{r})\delta(r-a) \ , \tag{4.3}$$

where the first term represents the instantaneous absorption of particles produced inside the sink and the surface density $\sigma_\omega(\mathbf{r}) = D_0(\partial c_\omega/\partial r)\,|_{r=a+}$ is determined by the source density outside the sink. Hence, the operators $Y_{\text{in}}(\omega)$ and $Y_{\text{ou}}(\omega)$ defined in Eqs. (2.17) become

$$Y_{\text{in}}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}')\theta(a - r') \ , \tag{4.4a}$$

$$Y_{\text{ou}}(\mathbf{r}, \mathbf{r}', \omega) = D_0 \delta(r-a) \frac{\mathbf{r}}{r} \times \nabla G_s(\mathbf{r}, \mathbf{r}', \omega)\theta(r'-a) \ . \tag{4.4b}$$

In the steady state case ($\omega = 0$) it is easy to find a compact expression for the operator $Y_{\text{ou}}(0)$. By the method of images

$$G_s(\mathbf{r}, \mathbf{r}', 0) = \frac{1}{4\pi D_0}\left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} - \frac{a}{r'}\frac{1}{|\mathbf{r} - (a/r')^2\mathbf{r}'|}\right], \quad \text{for } r, r' \geqslant a \ . \tag{4.5}$$

More generally, one finds by expanding the Green function in spherical harmonics

$$G_s(\mathbf{r}, \mathbf{r}', \omega) = \frac{2\mu}{\pi D_0}\sum_{lm}[i_l(\mu r)k_l(\mu a) - k_l(\mu r)i_l(\mu a)] \times \frac{k_l(\mu r')}{k_l(\mu a)} Y_{lm}(\theta, \varphi) Y^*_{lm}(\theta', \varphi') \quad (r < r') \ , \tag{4.6}$$

where $\mu = (-i\omega/D_0)^{1/2}$ and $i_l(\mu r)$ and $k_l(\mu r)$ are modified spherical Bessel functions.[10] This yields by substitution in Eq. (4.4b) the simple expression

$$Y(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}')\theta(a-r') + \delta(r-a)a^{-2} \times \sum_{lm}\frac{k_l(\mu r')}{k_l(\mu a)} Y_{lm}(\theta, \varphi) Y^*_{lm}(\theta', \varphi')\theta(r'-a) \ . \tag{4.7}$$

We may find the matrix element $\langle \mathbf{k} | T(\omega) | \mathbf{k} \rangle$ needed in Eq. (3.18) by calculating $\langle \mathbf{k} | Y(\omega) | \mathbf{k} \rangle$ and using Eq. (2.23). As an intermediate step we evaluate the local absorption $a_{\mathbf{k},\omega}(\mathbf{r})$ due to a plane wave source density $s_\omega(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})$. This is given by

$$\begin{aligned} a_{\mathbf{k},\omega}(\mathbf{r}) &= Y(\omega)\,|\mathbf{k}\rangle \\ &= \theta(a-r)\exp(i\mathbf{k}\cdot\mathbf{r}) + \delta(r-a)\frac{1}{k^2+\mu^2}\sum_{l=0}^{\infty}(2l+1) \\ &\quad \times i^l\left[\mu j_l(ka)\frac{k_{l+1}(\mu a)}{k_l(\mu a)} - kj_{l+1}(ka)\right]P_l(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}) \ , \end{aligned} \tag{4.8}$$

where $j_l(x)$ is a spherical Bessel function. Hence, one finds by straightforward calculation

$$\left\langle \mathbf{k} \middle| Y(\omega) \middle| \mathbf{k} \right\rangle = \frac{4\pi}{3}a^3 + \frac{4\pi D_0 a^2}{-i\omega + D_0 k^2} \times \sum_{l=0}^{\infty}(2l+1)j_l(ka)\left[\mu j_l(ka)\frac{k_{l+1}(\mu a)}{k_l(\mu a)} - kj_{l+1}(ka)\right] \ , \tag{4.9}$$

which is equivalent to the expression (A8) derived by Bixon and Zwanzig[5] for $\langle \mathbf{k} | T(\omega) | \mathbf{k} \rangle$. It is evident in the above derivation that the first term arises from instantaneous absorption inside the sinks. Having investigated the properties of a single perfect sink, we can now use these results in the average equations derived in the previous section.

V. AVERAGE EQUATION FOR PERFECT SINK SYSTEM

We consider first the case of spatially uniform sink density. Using Eqs. (2.23) and (4.9), we find upon substitution in Eq. (3.18)

$$\begin{aligned} -i\omega C_{\mathbf{k},\omega} = {} & -D_0 k^2 C_{\mathbf{k},\omega} - [\phi(-i\omega + D_0 k^2) \\ & + nt_{\text{ou}}(\mathbf{k}, \mathbf{k}, \omega)]C_{\mathbf{k},\omega} + s_{\mathbf{k},\omega} \ , \end{aligned} \tag{5.1}$$

where $\phi = (4\pi/3)na^3$ is the volume fraction occupied by sinks and $t_{\text{ou}}(\mathbf{k}, \mathbf{k}, \omega)$ is given by

$$t_{\text{ou}}(\mathbf{k}, \mathbf{k}, \omega) = 4\pi D_0 a^2 \sum_{l=0}^{\infty}(2l+1)j_l(ka) \times \left[\mu j_l(ka)\frac{k_{l+1}(\mu a)}{k_l(\mu a)} - kj_{l+1}(ka)\right] \ . \tag{5.2}$$

Clearly, the first term in square brackets in Eq. (5.1) must be combined with the terms describing free diffusion. Dividing by $(1+\phi)$ and keeping terms linear in n, we arrive at the modified average equation

$$-i\omega C_{\mathbf{k},\omega} = -D_0 k^2 C_{\mathbf{k},\omega} - nt_{\text{ou}}(\mathbf{k}, \mathbf{k}, \omega)C_{\mathbf{k},\omega} + (1-\phi)s_{\mathbf{k},\omega} \ . \tag{5.3}$$

In this equation the effect of the sinks on diffusion and absorption is described by only the relevant part of the T matrix. The source density is reduced, since only particles created outside the sinks can contribute to the average concentration. This interpretation makes it likely that consideration of higher order density terms in the average equation would lead to a factor $1 + \phi + \phi^2 + \cdots = (1-\phi)^{-1}$ multiplying $(-i\omega + D_0 k^2)C_{\mathbf{k},\omega}$, which upon division would precisely give the last term in Eq. (5.3). We emphasize that the above modification of the Foldy–Lax scheme is forced upon us by the physical interpretation. Equation (5.3) is the principal result of our analysis and isolates the effect of instantaneous absorption. This effect is accounted for by a modification of the source term and not via the propagator.

We now investigate whether the change from Eq. (3.18) to Eq. (5.3) has physical consequences. Consider for example a plane wave source density which is kept constant up to time $t=0$ and then switched off. The average particle density will vary as $C(\mathbf{r}, t)=C_{\mathbf{k}}(t) \times \exp(i\mathbf{k}\cdot\mathbf{r})$, with an amplitude $C_{\mathbf{k}}(t)$ which is constant for $t<0$ and decays to zero for $t>0$. According to Eq. (3.18) or (5.1), the initial amplitude is

$$C_{\mathbf{k}}(0)=[(1+\phi)D_0k^2+nt_{\mathrm{ou}}(\mathbf{k},\mathbf{k},0)]^{-1}s_{\mathbf{k}}\ , \tag{5.4}$$

whereas according to Eq. (5.3)

$$C'_{\mathbf{k}}(0)=[D_0k^2+nt_{\mathrm{ou}}(\mathbf{k},\mathbf{k},0)]^{-1}(1-\phi)s_{\mathbf{k}}\ , \tag{5.5}$$

where we use a prime to distinguish the two results. When expanded to first order in ϕ, both amplitudes are the same. However, by expanding one loses the important effect of screening.[2] We obtain an estimate of the screening length by expanding $t_{\mathrm{ou}}(\mathbf{k},\mathbf{k},0)=t_{\mathrm{ou}}^{(0)}+k^2t_{\mathrm{ou}}^{(2)}+O(k^4)$ in the denominators of Eqs. (5.4) and (5.5). This yields the two results

$$\xi^2=[(1+\phi)D_0+nt_{\mathrm{ou}}^{(2)}]/nt_{\mathrm{ou}}^{(0)}\ ,$$
$$\xi'^2=(D_0+nt_{\mathrm{ou}}^{(2)})/nt_{\mathrm{ou}}^{(0)}\ , \tag{5.6}$$

which become identical only if the terms linear in the density in the numerators are neglected. However, it should be possible to determine the effective diffusion coefficient correctly to first order in the density. We return to this question in the following sections.

Next consider the long-time behavior of the amplitude $C_{\mathbf{k}}(t)$. Asymptotically, the decay is dominated by a $\omega^{1/2}$ singularity in $t_{\mathrm{ou}}(\mathbf{k},\mathbf{k},\omega)$ leading to a $t^{-3/2}$ power law, as shown by Bixon and Zwanzig.[5] At intermediate times the decay of $C_{\mathbf{k}}(t)$ will be nearly exponential and slightly modified from the zero order diffusion. From Eq. (5.1) one finds for this intermediate time a decay rate

$$\Gamma(k)=D_0k^2+\frac{n}{1+\phi}t_{\mathrm{ou}}(\mathbf{k},\mathbf{k},0)\ , \tag{5.7}$$

whereas Eq. (5.3) yields

$$\Gamma'(\mathbf{k})=D_0k^2+nt_{\mathrm{ou}}(\mathbf{k},\mathbf{k},0)\ . \tag{5.8}$$

To linear order in n these results are identical.

We shall argue in the next sections that it is possible to consider separately the effects of diffusion and absorption in the macroscopic equation obtained by making a small gradient approximation. If we want to calculate the diffusion coefficient and the absorption coefficient correctly to terms linear in the density, then we are forced to make a choice between Eqs. (5.1) and (5.3). For the reasons given above we propose that Eq. (5.3) is the correct equation to employ.

To conclude this section we consider the generalization of Eq. (5.3) to spatially nonuniform sink density. Using the decomposition (2.16), we can write Eq. (3.11) in the form

$$A_\omega(\mathbf{r})=\nu(\mathbf{r})s_\omega(\mathbf{r})$$
$$+\int n(\mathbf{R}_1)T_{\mathrm{ou}}(\mathbf{r},\mathbf{r}',\omega;\mathbf{R}_1)c_\omega^{\mathrm{ex}}(\mathbf{r}')d\mathbf{r}'\,d\mathbf{R}_1\ , \tag{5.9}$$

where

$$\nu(\mathbf{r})=\int n(\mathbf{R}_1)\theta(a-|\mathbf{r}-\mathbf{R}_1|)d\mathbf{R}_1\ . \tag{5.10}$$

For slowly varying sink density one has approximately

$$\nu(\mathbf{r})\approx\tfrac{4}{3}\pi a^3[n(\mathbf{r})+\tfrac{1}{10}a^2\nabla^2n(\mathbf{r})]\ . \tag{5.11}$$

Eliminating $C_\omega^{\mathrm{ex}}(\mathbf{r}')$ from Eq. (5.9) by use of Eq. (3.12) and substituting in Eq. (3.9), one obtains the modified average equation

$$-i\omega C_\omega(\mathbf{r})=D_0\nabla^2C_\omega(\mathbf{r})$$
$$-\int K_{\mathrm{ou}}(\mathbf{r},\mathbf{r}',\omega)C_\omega(\mathbf{r}')d\mathbf{r}'+[1-\nu(\mathbf{r})]s_\omega(\mathbf{r})\ , \tag{5.12}$$

where

$$K_{\mathrm{ou}}(\omega)=\int n(\mathbf{R}_1)T_{\mathrm{ou}}(\omega;\mathbf{R}_1)d\mathbf{R}_1\ . \tag{5.13}$$

Equation (5.12) differs nontrivially from Eq. (3.16). The difference is most obvious for the case where the sink density is only nonzero in a finite part of space and where $s_\omega(\mathbf{r})$ is nonvanishing only outside the whole sink system. In that case $\nu(\mathbf{r})s_\omega(\mathbf{r})=0$.

VI. MULTIPOLE EXPANSION

The kernel $K_{\mathrm{ou}}(\mathbf{r},\mathbf{r}',\omega)$ is sufficiently complex to make it awkward to use in situations with nonuniform macroscopic geometry. We therefore assume that the average concentration $C_\omega(\mathbf{r})$ varies sufficiently slowly that one can employ a small gradient approximation. We then apply a multipole expansion to the kernel $K_{\mathrm{ou}}(\omega)$ and keep only multipoles of low order. We call the resulting equation for $C_\omega(\mathbf{r})$ the "modified macroscopic equation." The derivation is entirely analogous to the derivation of Maxwell's equations from the microscopic field equations.[11]

For the sake of comparison we apply the multipole expansion to Eq. (3.16) as well as to Eq. (5.12). We write the local average absorption rate $A_\omega(\mathbf{r})$ appearing in Eq. (3.16) in the form

$$A_\omega(\mathbf{r})=4\pi D_0\int n(\mathbf{R}_1)\rho_\omega(\mathbf{r}-\mathbf{R}_1,\mathbf{R}_1)d\mathbf{R}_1\ , \tag{6.1}$$

where

$$\rho_\omega(\mathbf{r}-\mathbf{R}_1,\mathbf{R}_1)$$
$$=(4\pi D_0)^{-1}\int T(\mathbf{r}-\mathbf{R}_1,\mathbf{r}'-\mathbf{R}_1,\omega)C_\omega(\mathbf{r}')d\mathbf{r}' \tag{6.2}$$

is the average absorption at $\mathbf{r}$ due to a single sink centered at $\mathbf{R}_1$. The factor $4\pi D_0$ is included for later convenience. Correspondingly, we define $\rho'_\omega(\mathbf{r}-\mathbf{R}_1,\mathbf{R}_1)$ for Eq. (5.12) by the same expression (6.2) with T replaced by T_{ou}. By definition, $\rho_\omega(\mathbf{r}-\mathbf{R}_1,\mathbf{R}_1)$ and $\rho'_\omega(\mathbf{r}-\mathbf{R}_1,\mathbf{R}_1)$ vanish for $|\mathbf{r}-\mathbf{R}_1|>a$. Multiplying by a smooth test function $f(\mathbf{r})$, integrating over $\mathbf{r}$, and expanding $f(\mathbf{r})$ about $\mathbf{R}_1$, one finds

$$\int f(\mathbf{r})\rho_\omega(\mathbf{r}-\mathbf{R}_1,\mathbf{R}_1)d\mathbf{r}=\sum_{n=0}^{\infty}\boldsymbol{\mu}_\omega^{(n)}(\mathbf{R}_1)\vdots(\partial/\partial\mathbf{R}_1)^nf(\mathbf{R}_1)\ , \tag{6.3}$$

where the Cartesian multipole moments $\boldsymbol{\mu}_\omega^{(n)}(\mathbf{R}_1)$ are defined by

$$\boldsymbol{\mu}_\omega^{(n)}(\mathbf{R}_1)=\frac{1}{n!}\int(\mathbf{r}-\mathbf{R}_1)^n\rho_\omega(\mathbf{r}-\mathbf{R}_1,\mathbf{R}_1)d\mathbf{r}\ , \tag{6.4}$$

with $(\mathbf{r}-\mathbf{R}_1)^n$ a polyadic tensor of rank n. Equivalently, we may write

$$\rho_\omega(\mathbf{r}-\mathbf{R}_1, \mathbf{R}_1)=\sum_{n=0}^{\infty}(-1)^n \mu_\omega^{(n)}(\mathbf{R}_1) \vdots \nabla^n \delta(\mathbf{r}-\mathbf{R}_1) , \qquad (6.5)$$

as can be seen by substitution in Eq. (6.3) and integration by parts. Hence, the local average absorption rate can be written

$$A_\omega(\mathbf{r})=4\pi D_0 \sum_{n=0}^{\infty}(-1)^n \nabla^n \vdots \mathbf{P}_\omega^{(n)}(\mathbf{r}) , \qquad (6.6)$$

where

$$\mathbf{P}_\omega^{(n)}(\mathbf{r})=n(\mathbf{r}) \mu_\omega^{(n)}(\mathbf{r}) \qquad (6.7)$$

is the local multipole density. For brevity we denote the monopole and dipole density by

$$\mathbf{P}_\omega^{(0)}(\mathbf{r})=Q_\omega(\mathbf{r})=n(\mathbf{r}) q_\omega(\mathbf{r}) ,$$

$$\mathbf{P}_\omega^{(1)}(\mathbf{r})=\mathbf{P}_\omega(\mathbf{r})=n(\mathbf{r}) \mathbf{p}_\omega(\mathbf{r}) . \qquad (6.8)$$

It follows from Eqs. (6.2) and (6.4) that the various multipole densities are related nonlocally to the average particle concentration. We find in particular for the monopole moment

$$q_\omega(\mathbf{R}_1)=\int \chi(\mathbf{R}_1-\mathbf{r}', \omega) C_\omega(\mathbf{r}') d\mathbf{r}' , \qquad (6.9)$$

where

$$\chi(\mathbf{R}_1-\mathbf{r}', \omega)=(4\pi D_0)^{-1} \int T(\mathbf{r}-\mathbf{R}_1, \mathbf{r}'-\mathbf{R}_1, \omega) d\mathbf{r} . \qquad (6.10)$$

Using the multipole expansion (6.6), we replace the average equation (3.16) by a macroscopic equation in which only the first few multipoles are kept. Keeping only terms relevant to second order in the gradients, we obtain the macroscopic equation

$$-i\omega C_\omega(\mathbf{r})=D_0 \nabla^2 C_\omega(\mathbf{r}) - 4\pi D_0[Q_\omega(\mathbf{r})-\nabla \cdot \mathbf{P}_\omega(\mathbf{r})+\nabla\nabla : \mathbf{P}_\omega^{(2)}(\mathbf{r})]+s_\omega(\mathbf{r}) \qquad (6.11)$$

together with the constitutive equations

$$Q_\omega(\mathbf{r})=n(\mathbf{r})[\gamma(\omega) C_\omega(\mathbf{r})+\epsilon(\omega) \nabla^2 C_\omega(\mathbf{r})] ,$$

$$\mathbf{P}_\omega(\mathbf{r})=\alpha(\omega) n(\mathbf{r}) \nabla C_\omega(\mathbf{r}) ,$$

$$\mathbf{P}_\omega^{(2)}(\mathbf{r})=\beta(\omega) n(\mathbf{r}) C_\omega(\mathbf{r}) \mathbf{1} , \qquad (6.12)$$

with coefficients given by

$$\gamma(\omega)=(4\pi D_0)^{-1} \int T(\mathbf{r}, \mathbf{r}', \omega) d\mathbf{r}\, d\mathbf{r}' ,$$

$$\alpha(\omega)=\tfrac{1}{3}(4\pi D_0)^{-1}\, Tr \int \mathbf{r}\mathbf{r}' T(\mathbf{r}, \mathbf{r}', \omega) d\mathbf{r}\, d\mathbf{r}' ,$$

$$\beta(\omega)=\tfrac{1}{6}(4\pi D_0)^{-1} \int r^2 T(\mathbf{r}, \mathbf{r}', \omega) d\mathbf{r}\, d\mathbf{r}' ,$$

$$\epsilon(\omega)=\tfrac{1}{6}(4\pi D_0)^{-1} \int r'^2 T(\mathbf{r}, \mathbf{r}', \omega) d\mathbf{r}\, d\mathbf{r}' . \qquad (6.13)$$

We have used the spherical symmetry of the sinks. From the symmetry of $T(\mathbf{r}, \mathbf{r}', \omega)$ it follows that $\beta(\omega)=\epsilon(\omega)$.

Similarly, the modified average equation (5.12) yields the modified macroscopic equation

$$-i\omega C_\omega(r)=D_0 \nabla^2 C_\omega(\mathbf{r}) - 4\pi D_0[Q_\omega'(\mathbf{r})-\nabla \cdot \mathbf{P}_\omega'(\mathbf{r})+\nabla\nabla : \mathbf{P}_\omega^{(2)\prime}(\mathbf{r})]+[1-\nu(\mathbf{r})] s_\omega(\mathbf{r}) \qquad (6.14)$$

together with constitutive equations like Eq. (6.12) with coefficients $\gamma_{ou}(\omega)$, $\alpha_{ou}(\omega)$, $\beta_{ou}(\omega)$, and $\epsilon_{ou}(\omega)$ which are defined as in Eq. (6.13) with $T(\mathbf{r}, \mathbf{r}', \omega)$ replaced by $T_{ou}(\mathbf{r}, \mathbf{r}', \omega)$.

VII. MACROSCOPIC EQUATIONS

The various terms in the modified macroscopic equation (6.14) have a direct physical interpretation. The term $\nu(\mathbf{r}) s_\omega(\mathbf{r})$ describes the instantaneous absorption of particles created inside the sinks. From Eqs. (5.9), (6.1), and (6.5) it is evident that the monopole density $Q_\omega'(\mathbf{r})$ describes the total average absorption by sinks centered at $\mathbf{r}$ of particles created outside the sinks. By integrating $Q_\omega'(\mathbf{r})$ over a volume V, one finds the total absorption of diffusing particles due to sinks with their centers inside V. Since the dipole and quadrupole density occur with a divergence, integration of these terms gives rise to a surface term which cancels for neighboring volume elements. If the entire surface of V lies in a region where $n(\mathbf{r})$ vanishes, then these terms do not contribute to the total absorption. Hence, $\mathbf{P}_\omega'(\mathbf{r}) - \nabla \cdot \mathbf{P}_\omega^{(2)\prime}(\mathbf{r})$ is more conveniently included with the macroscopic current density

$$\mathbf{J}_\omega'(\mathbf{r})=-D_0[\nabla C_\omega(\mathbf{r})+4\pi \mathbf{P}_\omega'(\mathbf{r})-4\pi \nabla \cdot \mathbf{P}_\omega^{(2)\prime}(\mathbf{r})] . \qquad (7.1)$$

Evidently, this differs from the average current density $\langle j_\omega(\mathbf{r})\rangle=-D_0 \nabla C_\omega(\mathbf{r})$. Substituting the constitutive equations, one finds

$$\mathbf{J}_\omega'(\mathbf{r})=-D_0[\nabla C_\omega(\mathbf{r}) + 4\pi n \alpha_{ou}(\omega) \nabla C_\omega(\mathbf{r})-4\pi \beta_{ou}(\omega) \nabla(n C_\omega)] . \qquad (7.2)$$

In a region with spatially uniform $n(\mathbf{r})$ this leads to the definition of the diffusion coefficient

$$D'(\omega)=D_0\{1+4\pi n[\alpha_{ou}(\omega)-\beta_{ou}(\omega)]\} . \qquad (7.3)$$

We can give a similar interpretation of the terms in the macroscopic equation (6.11), with the difference that now the monopole density $Q_\omega(\mathbf{r})$ includes a contribution from particles absorbed instantaneously inside the sinks, and that $\mathbf{P}_\omega(\mathbf{r})$ and $\mathbf{P}_\omega^{(2)}(\mathbf{r})$ include similar contributions. It seems unphysical to count the latter as part of a macroscopic current density $\mathbf{J}_\omega(\mathbf{r})$ of particles diffusing outside the sinks.

To illustrate the difference between the two macroscopic equations we calculate the various polarizabilities defined in Eq. (6.13) and the corresponding quantities with subscript ou. By putting $\mathbf{k}=0$ in Eq. (4.9) and using Eq. (2.23), one finds immediately

$$\gamma(\omega)=\tfrac{1}{3}\mu^2 a^3+\gamma_{ou}(\omega), \quad \gamma_{ou}(\omega)=a(1+\mu a) , \qquad (7.4)$$

where $\mu=(-i\omega/D_0)^{1/2}$. The coefficients $\alpha(\omega)$ and $\beta(\omega)$ follow from Eq. (4.8) by expanding the plane wave and evaluating the appropriate integrals. One finds

$$\alpha(\omega)=\tfrac{1}{15} \mu^2 a^5+\alpha_{ou}(\omega), \quad \alpha_{ou}(\omega)=a^3 \frac{1+\mu a+\frac{1}{3}\mu^2 a^2}{1+\mu a} ,$$

$$\beta(\omega)=\tfrac{1}{30} \mu^2 a^5+\beta_{ou}(\omega), \quad \beta_{ou}(\omega)=\tfrac{1}{6} a^3(1+\mu a) . \qquad (7.5)$$

Finally, we note that the kernel $\chi(\mathbf{r}-\mathbf{r}', \omega)$ defined in Eq. (6.10) is also easily found from Eq. (4.8) via the matrix element $\langle 0 | Y(\omega) | \mathbf{k} \rangle$. For its Fourier transform one finds

$$\begin{aligned}\hat{\chi}(\mathbf{k}, \omega) &= \int \chi(\mathbf{r}, \omega) \exp(i\mathbf{k}\cdot\mathbf{r}) d\mathbf{r} \\ &= (k^2+\mu^2)(a^2/k) j_1(ka) \\ &\quad + a j_0(ka)(1+\mu a) - k a^2 j_1(ka) \ , \end{aligned} \tag{7.6}$$

so that

$$\begin{aligned}\chi(\mathbf{r}-\mathbf{r}', \omega) &= \frac{1}{4\pi D_0}\theta(a - |\mathbf{r}-\mathbf{r}'|)(-i\omega - D_0\nabla'^2) \\ &+ \frac{1+\mu a}{4\pi a}\delta(|\mathbf{r}-\mathbf{r}'| - a) + \frac{1}{4\pi}\theta(a - |\mathbf{r}-\mathbf{r}'|)\nabla'^2 \ . \end{aligned} \tag{7.7}$$

Here the first term corresponds to the instantaneous absorption. From the coefficient of k^2 in the expansion of $\hat{\chi}(\mathbf{k}, \omega)$ one finds

$$\begin{aligned}\epsilon(\omega) &= \tfrac{1}{30}\mu^2 a^5 - \tfrac{1}{3}a^3 + \epsilon_{\mathrm{ou}}(\omega) \ , \\ \epsilon_{\mathrm{ou}}(\omega) &= \tfrac{1}{6}a^3(1+\mu a) + \tfrac{1}{3}a^3 \ . \end{aligned} \tag{7.8}$$

Note that $\epsilon(\omega) = \beta(\omega)$ as demanded by the symmetry of the T matrix, but that $\epsilon_{\mathrm{ou}}(\omega) \neq \beta_{\mathrm{ou}}(\omega)$. It is easily checked that the instantaneous absorption terms in Eq. (6.11) agree with Eq. (5.1).

Finally, we write the modified macroscopic equations obtained by substituting the constitutive equations into Eq. (6.14). It reads

$$\begin{aligned}-i\omega C_\omega(\mathbf{r}) &= D_0 \nabla \cdot [\nabla C_\omega + 4\pi n \alpha_{\mathrm{ou}}(\omega) \nabla C_\omega - 4\pi \beta_{\mathrm{ou}}(\omega) \nabla (n C_\omega)] \\ &- 4\pi D_0 n [\gamma_{\mathrm{ou}}(\omega) C_\omega + \epsilon_{\mathrm{ou}}(\omega)\nabla^2 C_\omega] + [1 - \nu(\mathbf{r})] s_\omega(\mathbf{r}) \ . \end{aligned} \tag{7.9}$$

The first term on the right describes the diffusion as affected by the presence of sinks and the second term describes the absorption. The frequency dependence of the coefficients gives rise to memory effects.

VIII. CONCLUSION

We have shown that the average diffusion–absorption equation for particles diffusing in a system of perfect sinks, when derived to first order in the sink density, is not given by the Foldy–Lax scheme, but by a modification thereof. There is a corresponding modification in the macroscopic equation which follows from the average equation by multipole expansion and restriction to second order spatial gradients.

Next we compare with some of the interesting results obtained by Bixon and Zwanzig[5] for a spatially uniform system of perfect sinks. These authors calculate the Green function (3.20) and for long times deduce an effective diffusion coefficient $D_{\mathrm{BZ}} = D_0(1+\phi)$. Equivalently, we can derive this D_{BZ} as the coefficient of k^2 in the expansion of $\Gamma(k)$ in Eq. (5.7). To linear order in n this yields

$$\begin{aligned}D_{\mathrm{BZ}} &= D_0 + n t_{\mathrm{ou}}^{(2)}(0) \\ &= D_0\{1 + 4\pi n[\alpha_{\mathrm{ou}}(0) - \beta_{\mathrm{ou}}(0) - \epsilon_{\mathrm{ou}}(0)]\} \\ &= D_0[1 + 4\pi n(a^3 - \tfrac{1}{6}a^3 - \tfrac{1}{2}a^3)] \\ &= D_0(1+\phi) \ , \end{aligned} \tag{8.1}$$

where we have used Eqs. (7.5) and (7.8). Note that nonlocal effects in the absorption contribute via $\epsilon_{\mathrm{ou}}(0)$ to D_{BZ}. The modified equation (5.8) yields the same result.

In the static case Bixon and Zwanzig define the effective diffusion coefficient $D_{\mathrm{BZ}}^{\mathrm{st}}$ as the coefficient of k^2 in the inverse of the Green function (3.20). From Eqs. (2.23) and (4.9) one finds

$$D_{\mathrm{BZ}}^{\mathrm{st}} = D_0(1+2\phi) \ . \tag{8.2}$$

The same result can also be obtained from Eqs. (6.11) and (6.12). In this way one finds

$$\begin{aligned}D_{\mathrm{BZ}}^{\mathrm{st}} &= D_0\{1 + 4\pi n[\alpha(0) - \beta(0) - \epsilon(0)]\} \\ &= D_0[1 + 4\pi n(a^3 - \tfrac{1}{6}a^3 - \tfrac{1}{6}a^3)] \\ &= D_0(1+2\phi) \ . \end{aligned} \tag{8.3}$$

To this effective diffusion coefficient there are contributions from instantaneous absorption inside the sinks in addition to absorption of particles created outside, already contained in Eq. (8.1).

We previously derived[2] in the static case a diffusion coefficient $D = D_0(1+3\phi)$. This must be compared with Eq. (7.3), which yields

$$D'(0) = D_0[1 + 4\pi n(a^3 - \tfrac{1}{6}a^3)] = D_0(1 + \tfrac{5}{2}\phi) \ . \tag{8.4}$$

In our previous work the quadrupole contribution $-\frac{1}{6}a^3$ was not included. We have argued above that the instantaneous absorption should be handled separately and that the coefficient governing the average diffusion is given by the result (8.4).

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