

On the sink strength and permeability of micro-cracked arrays†

BY KONSTANTIN Z. MARKOV

Faculty of Mathematics and Informatics, 'St. Kliment Ohridski' University of Sofia, 5 blvd J. Bourchier, BG-1164 Sofia, Bulgaria

Received 15 August 2002; accepted 8 October 2002

The effective absorption coefficient (the sink strength or the trapping constant) γ of a statistically isotropic random array of penny-shaped cracks is considered. The cracks are treated as oblate spheroids with vanishing aspect ratio. A variational procedure, based on Rubinstein-Torquato's principle is employed which yields non-trivial lower bounds on γ using appropriate trial fields of 'particle' and 'surface' type. The bounds include the crack density parameter for the array as well as the two-point correlation function for the set of crack's centers. The bounds also provide useful and nontrivial information concerning crack's competition at non-dilute concentration. The straightforward 'transition' of the obtained results as upper bounds on the effective permeability of an array of randomly distributed disk-like obstacles is finally indicated.

Keywords: micro-cracked media; absorption problem; permeability; variational estimates; effective properties

1. Introduction

An array of geometrically identical entities (particles or voids) that constitute phase 1 is immersed into an unbounded matrix (phase 2). The centers of the entities, to be called particles for definiteness in what follows, form a random set, assumed statistically homogeneous and isotropic. The particles act as ideal absorbers (sinks) for a diffusing species generated at a constant rate K in the matrix. In the steady-state limit, the governing equations of this well-known problem read

$$\Delta c(x) + K = 0, \quad x \in \mathcal{K}_2, \quad c(x) \Big|_{\partial\mathcal{K}_2} = 0, \quad (1.1)$$

where \mathcal{K}_2 is the region occupied by the matrix. The creation of defects is exactly compensated by their removal from the sinks, so that, in the steady-state limit under study,

$$\gamma \langle c(x) \rangle = K(1 - \eta_1). \quad (1.2)$$

The rate constant γ is the effective absorption coefficient (the sink strength or the trapping constant) of the medium. In (1.2), η_1 is the volume fraction of the sinks; the brackets $\langle \rangle$ denote ensemble averaging.

† Adapted from *Proc. Roy. Soc. Lond. A*, **459** (2003), 1135–1151, with several misprints corrected.

For a dilute array of spherical particles, γ was first evaluated by Smoluchowski, whose work initiated an extensive research of the so-called diffusion-controlled reactions in the context of heterogeneous catalysis or irradiation damage (see, for example, Brailsford & Bullough (1981) or Calef & Deutch (1983) for more details and references). For non-dilute concentrations, however, the sink interactions become predominant and their influence on the effective sink strength has been studied theoretically by many authors since the 1970s (see, for example, Doi 1976, Felderhof & Deutch 1976, Talbot & Willis 1980, Torquato & Rubinstein 1989). These authors addressed either various approximations or variational bounds on γ that utilize statistical information about spatial location of the sinks. In all of these works the shape of the absorbers was assumed, similarly to Smoluchowski, to be spherical. Only in Miller *et al.* (1991) absorption by a dilute array of oriented spheroids was studied together with the limiting cases when the latter degenerate into disks or rod-like inclusions (see also Torquato 2002).

In the present work the sinks will be taken as identical penny-shaped cracks of radius a . They are randomly distributed throughout the matrix and their orientation and location are uncorrelated. The cracks are treated as a limiting case of spheroids with semiaxes a and c when the aspect ratio $w = c/a \rightarrow 0$ (the ‘crack’ limit). Since the absorption is a ‘surface’ phenomenon in the sense that it takes place on the interfacial boundaries, the effective sink strength should ‘survive’ and not vanish after taking this limit, though its value would considerably differ, presumably, from that of an array of spheres. The obtained results (§§ 5–7) will corroborate and quantify these expectations. Moreover, in this way some useful information concerning cracks competition at non-dilute concentration will be obtained.

The straightforward ‘transition’ of the sink strength results as estimates on the effective permeability arrays of randomly distributed disk-like obstacles will be finally indicated in §8.

2. Statistical description of the micro-cracked medium

Consider a random array \mathcal{S} of identical and nonoverlapping spheroids, assumed both homogeneous and isotropic statistically. The spheroids are oblate with semiaxes $a = b > c$. Let x_j be the centers of the spheroids. We shall treat \mathcal{S} as a marked system of random points x_j , having imagined it constructed in the following manner.

Fix a ‘test’ spheroid S_0 at the origin O together with a Cartesian system $Ox_1x_2x_3$ along the semiaxes of S_0 and such that Ox_3 is along the shorter of them. Let e_1, e_2, e_3 be the unit vectors of the system $Ox_1x_2x_3$. Put a copy of the test spheroid S_0 at each of the points x_j and rotate it arbitrarily. The vector e_3 will then turn into the vector $\omega_j = U^j \cdot e_3$, where U^j is a unitary tensor, $\det U^j = 1$ (i.e., U^j is a ‘pure’ rotation in \mathbb{R}^3). Then attach ω_j to the point x_j as a ‘mark.’ The result is the marked system $\mathcal{S} = \{x_j, \omega_j\}$ of random points comprising the location $x_j \in \mathbb{R}^3$ of the j th spheroid center and its ‘orientation’ $\omega_j \in \Omega$; hereafter $\Omega = \{z \in \mathbb{R}^3 \mid |z| = 1\}$ denotes the unit sphere in \mathbb{R}^3 . The marked system \mathcal{S} represents mathematically the array of randomly oriented spheroids under study. (For the general definition and basic properties of sets of marked random points see Snyder (1975).)

The system \mathcal{S} is defined statistically by the multipoint probability densities F_k such that

$$dP = F_k(y_1, \dots, y_k; \omega_1, \dots, \omega_k) dy_1 \cdots dy_k dS_{\Omega_1} \cdots dS_{\Omega_k}$$

is the probability to find simultaneously in the vicinities $y_i < y < y_i + dy_i$ of the spatial positions y_i , k members of the system with marks (i.e. with orientations) $\omega \in \Omega$, whose end points lie in the vicinities dS_{Ω_i} of the points $\omega_i \in \Omega$, respectively ($i = 1, \dots, k$).

Observe that at $k = 1$ one has

$$F_1(y; \omega) = nP(\omega), \quad P(\omega) = \frac{1}{4\pi}, \quad (2.1)$$

where n is the number density of the spheroids. The adopted expression of $P(\omega)$ corresponds to the assumption that there is no preferable orientation of the latter.

Assume there is no long-range order in the array \mathcal{S} . Then

$$F_2(y_1, y_2; \omega_1, \omega_2) \rightarrow F_1(y_1; \omega_1)F_1(y_2; \omega_2) = n^2P(\omega_1)P(\omega_2)$$

as $|y_1 - y_2| \rightarrow \infty$, see (2.1). Hence, if the above mentioned rotations U^j in each point are mutually uncorrelated and there is no correlation between U^j and the location x_j of the spheroid, $j = 1, 2, \dots$, then the density function $F_2(y_1, y_2; \omega_1, \omega_2)$ factorizes as:

$$F_2(y_1, y_2; \omega_1, \omega_2) = n^2g(y_1 - y_2)P(\omega_1)P(\omega_2). \quad (2.2)$$

Here $f_2(y_1, y_2) = g(y_1 - y_2)n^2$ is the two-point density function for the random set of spheroid centers x_j and $g(|y_1 - y_2|)$ is the radial distribution function.

To forbid overlapping of the spheroids we assume also the simplest possible restriction on f_2 , namely:

$$f_2(y_1, y_2) = 0 \quad \text{if} \quad |y_1 - y_2| \leq 2a. \quad (2.3)$$

Note that the assumption (2.3) can be simply interpreted in the following manner. Insert each spheroid within a sphere of radius a , both having a common center. Eq. (2.3) then means that the so appearing spheres are impenetrable and hence their volume fraction is

$$\alpha = nV_a, \quad V_a = \frac{4}{3}\pi a^3; \quad (2.4)$$

recall that n is the number density of the spheroids. The quantity α will be used in what follows as the crack-density parameter after degeneration of the spheroids into cracks. Observe that the volume fraction, η_1 , of the spheroids is $\eta_1 = nV_\omega$, $V_\omega = \frac{4}{3}\pi a^2 c$. Due to (2.4), in the 'crack' limit, one has

$$\eta_1 = \alpha w \rightarrow 0 \quad \text{as} \quad w \rightarrow 0. \quad (2.5)$$

A convenient statistical description of the set \mathcal{S} , corresponding to the array of spheroids under study, is the marked random density function of the type of Stratonovich (1963),

$$\psi(x; \omega) = \sum_j \delta(x - x_j) \delta(\omega - \omega_j). \quad (2.6)$$

The moments of the field $\psi(x; \omega)$ can be expressed by the multipoint probability densities F_k and vice versa; the general formulae are given in Stratonovich (1963) (in the ‘non-marked’ case, but their generalization to the ‘marked’ one is straightforward). Under the assumptions (2.1) and (2.2), the first two moments of $\psi(x; \omega)$, needed in what follows, are

$$\left. \begin{aligned} \langle \psi(y; \omega) \rangle &= F_1(y; \omega) = nP(\omega), \\ \langle \psi(y_1; \omega_1) \psi(y_2; \omega_2) \rangle &= nP(\omega_1) \delta(y_1 - y_2) \delta(\omega_1 - \omega_2) \\ &\quad + n^2 g(y_1 - y_2) P(\omega_1) P(\omega_2). \end{aligned} \right\} \quad (2.7)$$

It is noted that the description of a dispersion of randomly oriented spheroids as a marked random point set was introduced in Markov (1998a) when bounding the effective thermal conductivity and elastic moduli of a micro-cracked solid.

3. The basic lemma

The micro-cracked solids are treated here, as already pointed out, as limiting cases of solids, containing spheroidal cavities when the aspect ratio $w = c/a \rightarrow 0$. In the quest for their effective behaviour one encounters certain quantities depending on the aspect ratio w , averaged over all possible orientations of the spheroids. The limits of these quantities when $w \rightarrow 0$, i.e. when the cavities degenerate into penny-shaped cracks, are then of central importance. The needed limits can be easily found, as it will be seen, making use of the following basic lemma.

Lemma 3.1. *Let $h(x; \omega)$ be the characteristic function of an ellipse (in two dimensions) or of a spheroid (in three dimensions) located at the origin, with the orientation ω . Then*

$$\left. \begin{aligned} \lim_{w \rightarrow 0} \frac{1}{w} \int_{\Omega} h(x; \omega) P(\omega) d\omega &= H(x), \\ H(x) &= \frac{b}{\rho} \sqrt{1 - \rho^2} h_a(x), \quad b = \begin{cases} \frac{2}{\pi}, & \text{in two dimensions,} \\ 1, & \text{in three dimensions,} \end{cases} \end{aligned} \right\} \quad (3.1)$$

where $h_a(x)$ is the characteristic function of a sphere of radius a , located at the origin, $\rho = r/a$, $r = |x|$.

Proof. Though only the three dimensional case will be needed in the sequel, the proposed proof needs first a study of the planar case.

Fix the Cartesian system Ox_1x_2 , with the center O in the ellipse’s center, see figure 1a. The orientation of the ellipse is then specified by the angle α_0 between e_ω (the direction of the shorter semiaxis) and Ox_1 , as shown in figure 1. Fix the point M and let $x = \overrightarrow{OM}$, $r = |x|$, $r < a$. The characteristic function $h(x; \omega) \neq 0$ for those angles α solely, for which the appropriate ellipses contain the point M . But in the limit $w \rightarrow 0$, when the ellipses become very prolate, such angles belong to the interval $(\alpha_0 - \Delta\alpha, \alpha_0 + \Delta\alpha) \cup (\alpha_0 + \pi - \Delta\alpha, \alpha_0 + \pi + \Delta\alpha)$, where

$$\Delta\alpha \approx \tan \Delta\alpha = \frac{d}{r} = \frac{c \sqrt{1 - r^2/a^2}}{r}, \quad (3.2)$$

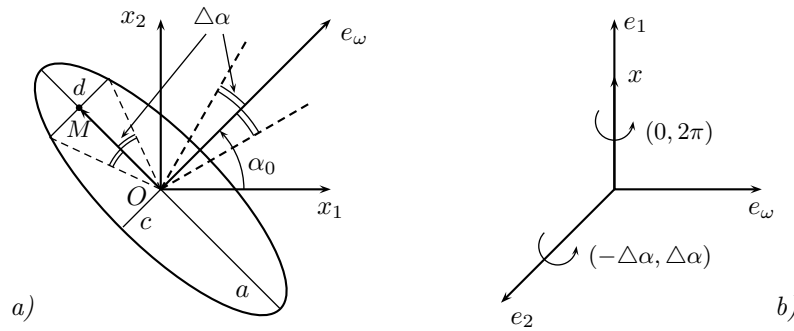


Figure 1. 'Geometrical' background of the derivation of (3.1)

see figure 1a for notations and the obvious geometrical sense of the above relations. Hence

$$\left. \begin{aligned} \frac{1}{w} \int_{\Omega} h(x; \omega) P(\omega) d\omega &\approx \frac{1}{2\pi c/a} 4\Delta\alpha \\ &\approx \frac{1}{2\pi c/a} \frac{4c\sqrt{1-r^2/a^2}}{r} = \frac{2}{\pi\rho} \sqrt{1-\rho^2}, \end{aligned} \right\} \quad (3.3)$$

which proves (3.1) in two dimensions, since the latter relation becomes exact in the limit $w \rightarrow 0$. (Observe that $P(\omega) = 1/(2\pi)$ in two dimensions.)

Consider now the three dimensional case. Fix a vector x , $|x| < a$, and consider all spheroids with a bigger axis along the unit vector e_1 , such that $e_1 \parallel x$, see figure 1b. Then $h(x, \omega) \neq 0$ for these spheroids. The vectors e_ω , corresponding to them, span the unit circle of length 2π in the plane perpendicular to e_1 , see figure 1b again. In turn, any of these spheroids can be rotated about the other of their bigger axes (the one along e_2 in figure 1b). As it follows from the foregoing two dimensional reasoning, the range of the appropriate angles of such rotations is the interval $(-\Delta\alpha, \Delta\alpha)$, see figure 1a, with $\Delta\alpha$ given in Eq. (3.2). (Note that we should not take into account now the opposite angles' interval $(\pi - \Delta\alpha, \pi + \Delta\alpha)$, since we have already counted the appropriate spheroids, having allowed the rotations about e_1 to span the unit circle.) That is why

$$\begin{aligned} \frac{1}{w} \int_{\Omega} h(x; \omega) P(\omega) d\omega &\approx \frac{1}{4\pi c/a} 2\pi \cdot 2\Delta\alpha \\ &\approx \frac{1}{c/a} \frac{\sqrt{1-r^2/a^2}}{r} = \frac{1}{\rho} \sqrt{1-\rho^2}, \end{aligned}$$

which proves (3.1) in three dimensions, since the latter relation becomes exact in the limit $w \rightarrow 0$. \square

Lemma 3.1 was formulated in Markov (1998a), when bounding the effective properties of micro-cracked solids, without proof. The reason was that the explicit form of $H(\rho)$ turned out needless there and only its property

$$\int_{\mathcal{V}_a} H(\rho) dx = V_a, \quad \mathcal{V}_a = \{x \mid |x| \leq a\}, \quad (3.4)$$

had to be employed. (Observe that it can be easily verified directly from (3.1), without needing the explicit expression of this function.) Unlike Markov (1998a) the explicit form of $H(\rho)$ will be needed here in §§5–7.

4. Variational procedure

Recall first the variational principle of Rubinstein and Torquato (1988), associated with the problem (1.1), (1.2).

Let \mathcal{A} be the class of smooth and statistically homogeneous trial fields such that

$$\mathcal{A} = \left\{ u(x) \mid \Delta u(x) + K = 0, x \in \mathcal{K}_2 \right\}. \quad (4.1)$$

Then

$$\gamma \geq \frac{K^2(1 - \eta_1)}{\langle I_2(x) |\nabla u(x)|^2 \rangle}. \quad (4.2)$$

The equality sign in (4.2) is achieved if $u(x) = c(x)$ is the actual field that solves the problem (1.1). In (4.2), $I_2(x)$ denotes the characteristic function of the region occupied by the matrix. Since the ‘crack’ limit will be of only interest, one can take $I_2(x) \equiv 1$ and $\eta_1 = 0$ (see (2.5)) from the very beginning here so that the bound (4.2) simplifies to

$$\gamma \geq \frac{K^2}{\langle |\nabla u(x)|^2 \rangle}. \quad (4.3)$$

5. The ‘particle-particle’ bound

Following Torquato & Rubinstein (1989), we shall first employ in (4.3) the trial field

$$u(x) = -\frac{K}{\eta_1} \int G(x-y) [I_1(y) - \eta_1] dy, \quad (5.1)$$

where $I_1(x)$ is the characteristic function of the spheroids (the sink phase 1) with volume concentration η_1 and $G(x) = 1/(4\pi|x|)$. Since $\Delta G(x) + \delta(x) = 0$, it is easily seen that $\Delta u(x) + K = 0$, if $x \in \mathcal{K}_2$, and therefore the fields $u(x)$ in (5.1) are indeed admissible.

For an array of spherical sinks the bound (4.3), corresponding to the trial field (5.1) was called by Torquato & Rubinstein (1989) ‘void’ (since the sinks are treated by these authors as voids in the medium throughout which the defects diffuse).

After Markov (2001) we prefer to call a bound of this type ‘particle-particle’ due to the fact that its evaluation (independently of any physical context) requires only the ‘particle-particle’ correlation, i.e., the probability density that two points thrown at random both fall within the particulate phase, imagined here as an array of very thin oblate ellipsoids.

To evaluate the bound (4.3), corresponding to the trial fields (5.1) in the crack limit, express first the field $I'_1(y) = I_1(y) - \eta_1$ in the integrand of (5.1) by means of the random density field (2.6)

$$I'_1(y) = \iint h(y-z; \omega) \psi'(z; \omega) dz d\omega, \quad (5.2)$$

where

$$\psi'(z; \omega) = \psi(z; \omega) - \frac{1}{2}nP(\omega)$$

is the fluctuating part of the field $\psi(z; \omega)$, so that $\langle \psi'(z; \omega) \rangle = 0$, see (2.7). (Observe that $I'_1(y)$ is the fluctuating part of $I_1(y)$.) If not explicitly indicated, the integration hereafter with respect to spatial coordinates is over the whole \mathbb{R}^3 , and that with respect to the 'mark,' i.e., spheroid's orientation, over the unit sphere Ω .

In virtue of (5.2) the quantity $\langle |\nabla u(x)|^2 \rangle$ that is of primary interest, as far as the bound (4.3) is concerned, reads

$$\left. \begin{aligned} \langle |\nabla u(x)|^2 \rangle &= \frac{1}{\eta_1^2} \iiint \nabla \varphi(z_1; \omega_1) \cdot \nabla \varphi(z_2; \omega_2) \\ &\times \langle \psi'(z_1; \omega_1) \psi'(z_2; \omega_2) \rangle \, dz_1 dz_2 \, d\omega_1 d\omega_2, \end{aligned} \right\} \quad (5.3)$$

where

$$\varphi(z; \omega) = \int \frac{h(u; \omega)}{4\pi|z-u|} \, du \quad (5.4)$$

is the Newtonian potential of the spheroid with the characteristic function $h(u; \omega)$. Recall that $\varphi(z; \omega)$ solves the equation

$$\Delta \varphi(z; \omega) + h(z; \omega) = 0. \quad (5.5)$$

In the crack limit $w \rightarrow 0$ one has

$$\left. \begin{aligned} \langle |\nabla u(x)|^2 \rangle &= \frac{A}{\alpha^2}, \quad A = nA_1 + n^2A_2, \\ A_1 &= \lim_{w \rightarrow 0} \frac{1}{w^2} \iint |\nabla \varphi(z; \omega)|^2 P(\omega) \, dz \, d\omega, \\ A_2 &= \iint \nabla \Phi(z_1) \cdot \nabla \Phi(z_2) \nu_2(z_1 - z_2) \, dz_1 dz_2, \end{aligned} \right\} \quad (5.6)$$

having used (5.3), (2.7) and (2.5). Here

$$\Phi(z) = \lim_{w \rightarrow 0} \frac{1}{w} \int \varphi(z; \omega) P(\omega) \, d\omega \quad (5.7)$$

and $\nu_2(y) = g(y) - 1$ is the total (binary) correlation function for the set of crack's centers.

Consider first the coefficient A_1 . Integration by parts together with (5.5) yields

$$A_1 = \lim_{w \rightarrow 0} \frac{1}{w^2} \iint \left[\int \varphi(z; \omega) h(z; \omega) \, dz \right] P(\omega) \, d\omega. \quad (5.8)$$

The potential $\varphi(x; \omega)$ inside the spheroid is a quadratic function of the Cartesian coordinates z_1, z_2, z_3 along its axes

$$\varphi(z; \omega) = \frac{1}{2} (M_0 - M_\perp (z_1^2 + z_2^2) - Mz_3^2). \quad (5.9)$$

In the case of a thin spheroid the factors M 's have the asymptotics

$$\left. \begin{aligned} M &= 1 - \frac{\pi}{2}w + o(w), \quad M_\perp = \frac{\pi}{4}w + o(w), \\ M_0 &= 2M_\perp a^2 + Mc^2 = (2M_\perp + Mw^2) a^2 = \frac{\pi}{2}wa^2 + o(w), \end{aligned} \right\} \quad (5.10)$$

according to Muratov (1975). Hence

$$\left. \begin{aligned} 2 \int \varphi(z; \omega) h(z; \omega) dz &= M_0 V_\omega \\ - M_\perp \int (z_1^2 + z_2^2) h(z; \omega) dz + o(w^2) &= \frac{2}{5} \pi V_a w^2 a^2 + o(w^2), \end{aligned} \right\} \quad (5.11)$$

after elementary integration, with (5.9) and (5.10) taken into account. Thus

$$nA_1 = \frac{2}{5} \pi \alpha a^2, \quad (5.12)$$

as it follows from (2.5).

Consider next the coefficient A_2 . Note first that the function $\Phi(z)$ in its expression solves the equation

$$\Delta \Phi(z) + H(z) = 0, \quad (5.13)$$

see (5.7), (5.5) and (3.1). Integration by parts, combined with (5.13), yields

$$A_2 = \iiint \Phi(z_1) H(z_2) \nu_2(z_1 - z_2) dz_1 dz_2 = \int S(x) \nu_2(x) dx. \quad (5.14)$$

Here $S(x)$ is the convolution

$$S(x) = (\Phi * H)(x) = \int \Phi(x - u) H(u) du \quad (5.15)$$

which as a consequence of (5.13) solves the equation

$$\Delta S(x) + (H * H)(x) = 0. \quad (5.16)$$

Split the total correlation as

$$\nu_2(y) = \nu_2^{\text{ws}}(y) + \tilde{\nu}_2(y), \quad \nu_2^{\text{ws}}(y) = -h_{2a}(y), \quad (5.17)$$

where $h_{2a}(y)$ is the characteristic function of a sphere of radius $2a$, located at the origin. The total correlation $\nu_2^{\text{ws}}(y)$ corresponds to the simplest well-stirred (hard spheres) distribution $g^{\text{ws}}(y) = 1 - h_{2a}(y)$. Note that

$$\tilde{\nu}_2(y) = 0, \quad \text{if } |y| \leq 2a, \quad (5.18)$$

due to the assumption (2.3). Accordingly, the coefficient A_2 splits as

$$A_2 = A_2^{\text{ws}} + \tilde{A}_2, \quad A_2^{\text{ws}} = - \int S(x) h_{2a}(x) dx, \quad \tilde{A}_2 = \int S(x) \tilde{\nu}_2(x) dx, \quad (5.19)$$

see (5.14) and (5.17).

The evaluation of A_2^{ws} is straightforward using the Fourier transform

$$\hat{f}(k) = \frac{1}{(2\pi)^{3/2}} \int e^{ik \cdot x} f(x) dx.$$

Then

$$A_2^{\text{ws}} = - \int \hat{S}(k) \hat{h}_{2a}(k) dk \quad \text{and} \quad \hat{S}(k) = \frac{(2\pi)^{3/2}}{k^2} \hat{H}^2(k),$$

due to (5.16). In spherical coordinates in the k -space the latter formula yields

$$A_2^{\text{ws}} = -\frac{4\pi}{a} (2\pi)^{3/2} \int_0^\infty \widehat{H}^2(\kappa) \widehat{h}_{2a}(\kappa) \, d\kappa, \quad \kappa = |k|a. \quad (5.20)$$

In turn, using the radial symmetry of both $H(x)$ and $h_{2a}(x)$, one has

$$\widehat{H}(k) = \frac{3V_a}{(2\pi)^{3/2}\kappa} \int_0^1 \rho H(\rho) \sin \kappa \rho \, d\rho, \quad \widehat{h}_{2a}(k) = \frac{3V_a}{(2\pi)^{3/2}} \frac{\sin 2\kappa - 2\kappa \cos 2\kappa}{\kappa^3}. \quad (5.21)$$

In virtue of (3.1),

$$\int_0^1 \rho H(\rho) \sin \kappa \rho \, d\rho = \int_0^1 \sqrt{1-\rho^2} \sin \kappa \rho \, d\rho = \frac{\pi}{2\kappa} H_1(\kappa),$$

where $H_1(\kappa)$ is the Struve function, see Abramowitz & Stegun (1972). Eventually,

$$A_2^{\text{ws}} = - \left[\frac{9}{2} \pi \int_0^\infty \frac{1}{\kappa^7} H_1^2(\kappa) (\sin 2\kappa - 2\kappa \cos 2\kappa) \, d\kappa \right] V_a^2 a^2. \quad (5.22)$$

The author was not able to find analytically the value of the integral in (5.22). However, numerical integration indicates that the value of the multiplier in the square bracket in (5.22) equals 28/15 within the accuracy of $1 \cdot 10^{-12}$. Since such an accuracy far exceeds any reasonable needs, one can take as ‘proven’ that the said multiplier is exactly 28/15. Thus

$$A_2^{\text{ws}} = -\frac{28}{15} V_a^2 a^2. \quad (5.23)$$

Consider finally the coefficient \widetilde{A}_2 , see (5.19). In virtue of (5.18), only the values of $S(x)$ at $|x| > 2a$ are needed for its evaluation. But the function $S(x)$ is harmonic at $|x| > 2a$. (The function $H(x)$ vanishes at $|x| > a$, see (3.1), and therefore the convolution $(H * H)(x) = 0$, if $|x| > 2a$.) The Poisson formula then yields

$$S(x) = \frac{1}{4\pi r} \int_{V_a} (H * H)(y) \, dy = \frac{V_a^2}{4\pi r}, \quad r = |x| > 2a,$$

cf. (3.4). (Observe that $S(x)$ is radially symmetric.) Hence

$$\left. \begin{aligned} \widetilde{A}_2 &= \int S(x) \widetilde{\nu}_2(x) \, dx = V_a^2 a^2 m_1, \\ m_1 &= \int_2^\infty \rho \widetilde{\nu}_2(\rho) \, d\rho, \quad \rho = r/a. \end{aligned} \right\} \quad (5.24)$$

It is noted that the same statistical quantity m_1 shows up in the bound on the sink strength in the case of spherical sinks, due to Talbot & Willis (1980), as well as in the ‘void’ bound of Torquato and Rubinstein (1989).

It remains to insert (5.6), (5.12), (5.23) and (5.24) into (4.3) to get eventually

$$\gamma a^2 \geq \frac{\alpha}{\frac{\pi}{5} - \frac{28}{15}\alpha + m_1 \alpha}. \quad (5.25)$$

6. The ‘surface-surface’ bound

Let $h_\tau(x, \omega)$ be the characteristic function of a spheroid with orientation ω , centered at the origin, whose semi-axes are $(1 + \tau)a$ and $(1 + \tau)c$, $\tau > 0$. Observe that the function

$$s(x, \omega) = \left. \frac{d}{d\tau} h_\tau(x, \omega) \right|_{\tau=0} \quad (6.1)$$

is proportional to the Dirac’s delta $\delta_S(x)$, whose support is the surface S_ω of the ellipsoid with the characteristic function $h(x, \omega)$. A similar observation of Doi (1976), in the case of spherical sinks, was the basis in Markov (2001) for derivation of a new ‘surface-surface’ bound on the sink strength as well as of a new and simpler derivation of the bound of Talbot and Willis (1980) within the frame of the variational principle (4.3) (Markov, 1998b).

Here we shall generalize the reasoning of the author (Markov, 2001) to the case of a micro-cracked solid, using (6.1) as a starting point.

Consider the function

$$J(x) = \iint s(x - y; \omega) \psi(y; \omega) dy d\omega \quad (6.2)$$

— this is the ‘surface’ counterpart of the field $I_1(x)$, defined in (5.2), since $J(x)$ is a superposition of delta functions concentrated on the surfaces of the ellipsoids that form the array under consideration, see (2.7).

The mean value of the field $J(x)$ is

$$\left. \begin{aligned} \langle J(x) \rangle &= n \frac{d}{d\tau} \int \left[\int h_\tau(x - y, \omega) dy \right] P(\omega) d\omega \Big|_{\tau=0} \\ &= n \frac{d}{d\tau} (1 - \tau)^3 \frac{4}{3} \pi a^2 c \Big|_{\tau=0} = 3\eta_1 = 3nV_a w, \end{aligned} \right\} \quad (6.3)$$

see (2.7).

Guided by (5.1), consider the trial field

$$u(x) = -\frac{K}{3\eta_1} \int G(x - y) [J(y) - 3\eta_1] dy, \quad (6.4)$$

which is obviously admissible, $\Delta u(x) = K$, $x \in \mathcal{K}_2$.

It is natural to call the bound, corresponding to the trial field (6.4), ‘surface-surface’ since it is generated by a superposition of delta’s, concentrated over the surfaces of the spheroids. Hence, when evaluating the bound the two-point probability that a pair of points, thrown at random, both ‘land’ on such surfaces will show up. This probability can be expressed through the radial distribution function $g(r)$ of the spheroid’s centers — something that will be tacitly done in the course of calculations below.

To find the explicit form of the ‘surface-surface’ bound note first that the random field in the integrand of (6.4) is just the fluctuating part of $J(x)$:

$$J'(x) = J(x) - 3\eta_1 = \iint s(x - y; \omega) \psi'(y, \omega) dy d\omega, \quad (6.5)$$

as a consequence of (6.2) and (6.3).

The scheme of §5 is now implemented in the ‘surface’ case under discussion. The quantity $\langle |\nabla u(x)|^2 \rangle$ has here the form

$$\left. \begin{aligned} \langle |\nabla u(x)|^2 \rangle &= \frac{1}{9\eta_1^2} \iiint \nabla \sigma(z_1; \omega_1) \cdot \nabla \sigma(z_2; \omega_2) \\ &\times \langle \psi'(z_1; \omega_1) \psi'(z_2; \omega_2) \rangle \, dz_1 dz_2 \, d\omega_1 d\omega_2, \end{aligned} \right\} \quad (6.6)$$

where the function

$$\sigma(z; \omega) = \int \frac{s(u; \omega)}{4\pi|z-u|} \, du \quad (6.7)$$

solves the equation

$$\Delta \sigma(z; \omega) + s(z; \omega) = 0. \quad (6.8)$$

Observe that

$$\sigma(z; \omega) = \left. \frac{d}{d\tau} \varphi_\tau(z; \omega) \right|_{\tau=0}, \quad (6.9)$$

where $\varphi_\tau = h_\tau * G$ is the Newtonian potential of the spheroid whose characteristic function is $h_\tau(x; \omega)$.

In the crack limit $w \rightarrow 0$ one has

$$\left. \begin{aligned} \langle |\nabla u(x)|^2 \rangle &= \frac{C}{9\alpha^2}, \quad C = nC_1 + n^2C_2, \\ C_1 &= \lim_{w \rightarrow 0} \frac{1}{w^2} \iint |\nabla \sigma(z; \omega)|^2 P(\omega) \, dz \, d\omega, \\ C_2 &= \iint \nabla \Psi(z_1) \cdot \nabla \Psi(z_2) \nu_2(z_1 - z_2) \, dz_1 dz_2, \end{aligned} \right\} \quad (6.10)$$

having used (6.6), (2.7) and (2.5). Here

$$\Psi(z) = \lim_{w \rightarrow 0} \frac{1}{w} \int \sigma(z; \omega) P(\omega) \, d\omega. \quad (6.11)$$

Let us start again with the coefficient C_1 . Integration by parts in its definition, with (6.1), (6.8) and (6.9) taken into account, yields

$$\begin{aligned} C_1 &= \lim_{w \rightarrow 0} \frac{1}{w^2} \int \left[\int \sigma(z; \omega) s(z; \omega) \, dz \right] P(\omega) \, d\omega \\ &= \lim_{w \rightarrow 0} \frac{1}{w^2} \int \left. \frac{d}{d\tau} \varphi_\tau(z, \omega) \right|_{\tau=0} \left. \frac{d}{d\tau} h_\tau(z, \omega) \right|_{\tau=0} \, dz. \end{aligned}$$

But

$$2\varphi_\tau(z, \omega) = 2\varphi(z, \omega) + \pi w a^2 \tau + o(w) + o(\tau)$$

(see (5.9) and (5.10)). Hence

$$\left. \frac{d}{d\tau} \varphi_\tau(z, \omega) \right|_{\tau=0} = \frac{1}{2} \pi w a^2 + o(w)$$

and therefore

$$\begin{aligned} \int \sigma(z; \omega) s(z; \omega) dz \Big|_{\tau=0} &= (\pi w a^2 + o(w)) \frac{d}{d\tau} \int h_\tau(z, \omega) dz \Big|_{\tau=0} \\ &= (\pi w a^2 + o(w)) \frac{d}{d\tau} (1 + \tau)^3 \frac{4}{3} \pi a^2 c \Big|_{\tau=0} = 3\pi w^2 V_a a^2 + o(w^2). \end{aligned}$$

Thus

$$nC_1 = \frac{3}{2} \pi \alpha a^2, \tag{6.12}$$

To find the coefficient C_2 , see (6.10), note first that the function $\Psi(z)$, defined in (6.11), solves the equation

$$\Delta \Psi(z) + T(z) = 0, \tag{6.13}$$

where

$$\left. \begin{aligned} T(z) &= \lim_{w \rightarrow 0} \frac{1}{w} \int s(z, \omega) P(\omega) d\omega \\ &= \lim_{w \rightarrow 0} \frac{1}{w} \frac{d}{d\tau} \int h_\tau(z, \omega) P(\omega) d\omega \Big|_{\tau=0} \\ &= \frac{d}{d\tau} H_\tau(z) \Big|_{\tau=0}, \quad H_\tau(z) = \frac{1 + \tau}{\rho} \sqrt{1 - \frac{\rho^2}{(1 + \tau)^2}}, \end{aligned} \right\} \tag{6.14}$$

see (3.1). Simple differentiation yields

$$T(z) = \frac{1}{\rho \sqrt{1 - \rho^2}} h_a(z), \quad \rho = |z|/a. \tag{6.15}$$

Note that

$$\int_{V_a} T(\rho) dx = 3V_a \tag{6.16}$$

which can be deduced directly from (6.14) as well.

The evaluation of C_2 now literally follows that of the coefficient A_2 in §5, see Eqs. (5.15) ÷ (5.24). The difference is that the function $H(z)$ from (3.1) is replaced by the function $T(z)$ found in (6.15). Namely, we write

$$C_2 = \iiint \Psi(z_1) T(z_2) \nu_2(z_1 - z_2) dz_1 dz_2 = \int U(x) \nu_2(x) dx, \tag{6.17}$$

where $U(x)$ is the convolution

$$S(x) = (\Psi * T)(x) = \int \Psi(x - u) T(u) du \tag{6.18}$$

which solves now the equation

$$\Delta U(x) + (T * T)(x) = 0, \tag{6.19}$$

as a consequence of (6.13). Then

$$C_2 = C_2^{\text{ws}} + \tilde{C}_2, \quad C_2^{\text{ws}} = - \int U(x) h_{2a}(x) dx, \quad \tilde{C}_2 = \int U(x) \tilde{\nu}_2(x) dx, \quad (6.20)$$

see (6.17) and (5.17).

The evaluation of the ‘well-stirred’ contribution C_2^{ws} is performed again by using Fourier transform technique. One should only note the formula

$$\int_0^1 \rho T(\rho) \sin \kappa \rho d\rho = \int_0^1 \frac{\sin \kappa \rho}{\sqrt{1-\rho^2}} d\rho = \frac{\pi}{2} H_0(\kappa),$$

where $H_0(\kappa)$ is the Struve function, this time of zeroth-order. Eventually

$$C_2^{\text{ws}} = - \left[\frac{9}{2} \pi \int_0^\infty \frac{1}{\kappa^5} H_0^2(\kappa) (\sin 2\kappa - 2\kappa \cos 2\kappa) d\kappa \right] V_a^2 a^2. \quad (6.21)$$

Numerical integration indicates that the value of the multiplier in the square bracket in (6.21) equals 16 within the accuracy of $1 \cdot 10^{-12}$. Hence one can take as ‘proven’ that

$$C_2^{\text{ws}} = -16V_a^2 a^2. \quad (6.22)$$

We note further that the function $U(x)$ is harmonic at $|x| > 2a$. (The function $T(x)$ vanishes at $|x| > a$, see (6.15), and therefore the convolution $(T * T)(x) = 0$, if $|x| > 2a$.) Hence

$$U(x) = \frac{1}{4\pi r} \int_{|y| \leq 2a} (T * T)(y) dy = \frac{9V_a^2}{4\pi r}, \quad r = |x| \geq 2a,$$

see (6.16), so that

$$\tilde{C}_2 = \int U(x) \tilde{\nu}_2(x) dx = 9V_a^2 a^2 m_1. \quad (6.23)$$

Here m_1 is the statistical quantity for the crack array defined in (5.24).

It remains to insert (6.10), (6.12), (6.22) and (6.23) into (4.3):

$$\gamma a^2 \geq \frac{\alpha}{\frac{1}{6}\pi - \frac{16}{9}\alpha + m_1\alpha} \quad (6.24)$$

which is the explicit form of the ‘surface-surface’ bound on the sink strength of a micro-cracked array.

7. A more general bound

One can try to improve on the bounds, obtained in §§5 and 6, by combining the trial fields used there, namely,

$$u(x) = -\frac{K}{\eta_1} \int G(x-y) [\lambda I_1(y) - \eta_1 + \frac{1}{3}\mu J_1(y)] dy. \quad (7.1)$$

The field (7.1) is obviously admissible, whatever the adjustable constants λ , μ . To get a finite value for the denominator $\langle |\nabla u(x)|^2 \rangle$ in (4.2) and hence a nontrivial

lower bound on γ , the integrand in (7.1) should have a zero mean value. This requires that

$$\lambda + \mu = 1, \quad (7.2)$$

see (6.3), which allows one to recast (7.1) as

$$u(x) = -\frac{K}{\eta_1} \int G(x-y) [\lambda I_1'(y) + \frac{1}{3}\mu J_1'(y)] dy. \quad (7.3)$$

Putting $\lambda = 1$, $\mu = 0$ in (7.3) reproduces the ‘particle’ field (5.1); accordingly, the choice $\lambda = 0$, $\mu = 1$ yields the ‘surface’ field (6.4). Hence the more general trial fields (7.3) should produce a lower bound on the effective sink strength γ superior to both bounds (5.25) and (6.24), if an appropriate optimization with respect to λ and μ is performed (under the constraint (7.2)).

For the field (7.3) the quantity $\langle |\nabla u(x)|^2 \rangle$ reads

$$\langle |\nabla u(x)|^2 \rangle = \frac{1}{\alpha^2} (\lambda^2 A + \frac{2}{3}\lambda\mu B + \frac{1}{9}\mu^2 C), \quad (7.4)$$

where A and C are defined in Eqs. (5.6) and (6.10), respectively, and B is a ‘mix’ between their definitions:

$$\left. \begin{aligned} \langle |\nabla u(x)|^2 \rangle &= \frac{B}{\alpha^2}, \quad B = nB_1 + n^2B_2, \\ B_1 &= \lim_{w \rightarrow 0} \frac{1}{w^2} \iint \nabla \varphi(z; \omega) \cdot \nabla \sigma(z; \omega) P(\omega) dz d\omega, \\ B_2 &= \iint \nabla \Phi(z_1) \cdot \nabla \Psi(z_2) \nu_2(z_1 - z_2) dz_1 dz_2, \end{aligned} \right\} \quad (7.5)$$

see (5.7), (5.4), (6.7), (6.11), (2.7) and (2.5).

The evaluation of the coefficients B_1 and B_2 in (7.5) literally follows the scheme, used in §§5–6 and the final results read

$$nB_1 = \pi\alpha a^2, \quad B_2 = \left(-\frac{82}{15} + 3m_1\right) V_a^2 a^2. \quad (7.6)$$

Note that the first term in the expression (7.6) for B_2 is the ‘well-stirred’ contribution which has the integral form

$$B_2^{\text{ws}} = - \left[\frac{9}{2}\pi \int_0^\infty \frac{1}{\kappa^6} H_0(\kappa) H_1(\kappa) (\sin 2\kappa - 2\kappa \cos 2\kappa) d\kappa \right] V_a^2 a^2. \quad (7.7)$$

cf. (5.22) and (6.21). Numerical integration indicates that the multiplier in (7.7) equals $82/15$ within the accuracy of $1 \cdot 10^{-12}$.

A straightforward minimization of the quadratic form (7.4), with the constraint (7.2) taken into account, yields

$$\gamma a^2 \geq \frac{\alpha}{\frac{1}{6}\pi - \frac{16}{9}\alpha - \frac{2}{135\pi}\alpha^2 + m_1\alpha} \quad (7.8)$$

see (4.2), and this represents a more restrictive lower bound on the sink strength γ of a micro-cracked solid.

It is noted that in the case of spherical sinks the foregoing procedure, employed by the author (Markov, 2001), yielded the known bound of Talbot & Willis (1980). That is why (7.8) can be viewed as a ‘crack’ counterpart of the latter bound.

Observe also that the only difference between (7.8) and (6.24) is the underlined term in the denominator of (7.8) which clearly is negligibly small. Hence the more general bound (7.8) practically brings forth no improvement as compared with the ‘surface’ bound (6.24).

8. Bounds on the effective permeability

Consider now a steady-state Stokesian flow of a viscous fluid through the array \mathcal{S} of ellipsoidal obstacles. The flow is described by the equations

$$\mu\Delta v(x) = \nabla p - e, \quad \nabla \cdot v = 0, \quad x \in \mathcal{K}_2, \quad v(x) \Big|_{\partial\mathcal{K}_2} = 0, \quad (8.1)$$

where v is the velocity, p the pressure, μ the viscosity and e is the applied pressure gradient. An important problem consists then in evaluating the permeability (or the Darcy constant) k of the array, defined as

$$\langle v \rangle = \mu k e. \quad (8.2)$$

Detailed discussion of this well-known problem can be found in Torquato (2000, 2002) together with an exhaustive list of appropriate references.

A variational principle for the flow problem (8.1) was introduced by Rubinstein & Torquato (1989) together with trial fields tantamount to ones used in the absorption problem. As it turned out the resulting bounds on the permeability k of a two-phase medium include the same statistical parameters as the bounds on the sink strength γ . Moreover,

$$\text{if } \gamma \geq \mathcal{L} \quad \text{then } k \leq \frac{2}{3}\mathcal{L}^{-1} \quad (8.3)$$

for the classes of trial fields used by these authors, see Torquato (2000, 2002). It is noted that the correspondence (8.3) was explicitly indicated by Doi (1976) within the frame of his variational procedure, clarified later on by Rubinstein & Torquato (1988, 1989). Hence one can immediately recast the bounds on the sink strength γ , found in §§5–7, as upper bounds on the permeability of a micro-cracked array to be viewed here as an array of disk-like obstacles. In particular, the most restrictive bound (7.8) on γ , when inserted into (8.3), yields

$$k \leq \frac{2a^2}{3\alpha} \left(\frac{1}{6}\pi - \frac{16}{9}\alpha - \frac{2}{135\pi}\alpha^2 + m_1\alpha \right). \quad (8.4)$$

For a dilute crack array, $n \ll 1$, the bound (8.4) gives

$$k = \frac{1}{12an} + o(n). \quad (8.5)$$

A simple check shows that (8.5) coincides with the dilute value of the permeability of an array of disk-like obstacles, as given by Torquato (2002), Eq. (19.115).

9. Discussion

For dilute crack fractions, $\alpha \ll 1$, the bounds (7.8) and (6.24) yield

$$\gamma \geq \gamma_s + o(n), \quad \gamma_s = 8an, \quad (9.1)$$

and hence they both produce the correct dilute limit, given by Miller *et al.* (1991), see also Torquato (2002), Eq. (19.58).

Unlike them the ‘particle’ bound (5.25) gives

$$\gamma \geq \frac{20}{3}an + o(n).$$

which underestimates the exact value γ_s . Recall that the same happens in the case of an array of spheres for which the ‘void’ bound of Torquato and Rubinstein (1989) does not produce either the respective Smoluchowski value $4\pi an$. At the same time, both ‘surface’ bound of Markov (2001) and the bound of Talbot & Willis (1980) reproduce correctly this value.

To compare, at least qualitatively, the sink ability of arrays of cracks and spheres (of the same radius a , located at the same points x_j), assume that the radial distribution function of the set x_j coincides with the familiar Percus-Yevick one. The statistical parameter m_1 , see (5.24), then reads

$$m_1 = \frac{\alpha(22 - \alpha)}{5(1 + 2\alpha)}, \quad (9.2)$$

according to Talbot and Willis (1980). The bound of the same authors for an array of spheres is extremely simple in this case

$$\gamma a^2 \geq \frac{3\alpha(1 + 2\alpha)}{(1 - \alpha)^2}. \quad (9.3)$$

For dilute α , the sink strength of the spheres is $\pi/2$ -times higher than the one for the cracks. For non-dilute sink fractions, however, the difference between spherical and crack-like absorbers becomes much more considerable. This can be explained by screening effects which should be more pronounced in the non-dilute crack arrays than in the respective arrays of spheres.

It is noted finally that the bound (7.8) allows one to propose the following approximation

$$\gamma a^2 \approx \frac{6}{\pi}\alpha + \frac{64}{\pi^2}\alpha^2 \quad (9.4)$$

for the sink strength of a micro-cracked array. It coincides to the order $o(\alpha^2)$ with the right-hand side of (7.8), independently of the statistics, since the radial distribution function affects only the α^3 -term in the power series expansion of the bound. For both well-stirred and Percus-Yevick distributions of the sink’s centers Eq. (9.4) provides an error of less than 4 %, if $\alpha \leq 0.2$, as compared with (7.8).

References

- Abramowitz, M. & Stegun, C. A. 1972 *Handbook of mathematical functions*, ch 12. New York: Dover.
- Brailsford, A. D. & Bullough, R. 1981 The theory of sink strengths. *Philos. Trans. Roy. Soc. Lond. A* **302**, 87–137.

- Calef, D. F. & Deutch J. M. 1983 Diffusion-controlled reactions. *A. Rev. Phys. Chem.* **34**, 493–523.
- Doi, M. 1976 A new variational approach to the diffusion and the flow problem in porous media. *J. Phys. Soc. Jpn* **40**, 567–572.
- Felderhof, B. U. & Deutch, J. M. 1976 Concentration dependence of the rate of diffusion-controlled reactions. *J. Chem. Phys.* **64**, 4551–4558.
- Markov, K. Z. 1998*a* On the cluster bounds on the effective properties of microcracked solids. *J. Mech. Phys. Solids* **46**, 357–388.
- Markov, K. Z. 1998*b* On the two-point correlation functions in random arrays of nonoverlapping spheres. *Annuaire Univ. Sofia, Fac. Math. Inf., Livre. 2, Mat. Appl. et Inf.* **91(1997)**, 151–175.
- Markov, K. Z. 2001 A new bound on the absorption coefficient of a two-phase medium. *Annuaire Univ. Sofia, Fac. Math. Inf.* **94/2000**, 123–131.
- Miller, C. A., Kim, I. C. & Torquato, S. 1991 Trapping and flow among random arrays of oriented inclusions. *J. Chem. Phys.* **94**, 5592 – 5598.
- Muratov, R. Z. 1975 *The potentials of an ellipsoid*, §4. Moscow: Atomizdat. (In Russian.)
- Rubinstein, J. & Torquato, S. 1988 Diffusion-controlled reactions: Mathematical formulation, variational principles, and rigorous bounds. *J. Chem. Phys.* **88**, 6372–6380.
- Rubinstein, J. & Torquato, S. 1989 Flow in random porous media: Mathematical formulation, variational principles, and rigorous bounds. *J. Fluid Mech.* **206**, 25–46.
- Snyder, D. 1975 *Random point processes*. Wiley.
- Stratonovich, R. L. 1963 *Topics in theory of random noises*. Vol. 1, New York: Gordon and Breach.
- Talbot, D. R. S. & Willis, J. R. 1980 The effective sink strength of a random array of voids in irradiated material. *Proc. R. Soc. London* **A370**, 351–374.
- Torquato, S. 2000 Diffusion-absorption and flow processes in disordered porous media. In *Heterogeneous media. Micromechanics modeling methods and simulation* (eds K. Z. Markov & L. Preziosi), pp. 163–240. Birkhäuser.
- Torquato, S. 2002 *Random heterogeneous materials: Microstructure and macroscopic properties*. Springer.
- Torquato, S. & Rubinstein, J. 1989 Diffusion-controlled reactions: II. Further bounds on the rate constant. *J. Chem. Phys.* **90**, 1644–1647.