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DIFFUSIONAL HOMOGENIZATION OF BINARY STRUCTURES COMPOSED OF ARRAYS OF DELTA-DOPED LAYERS IN HOST CRYSTALS

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Diffusion of dopants in crystalline structures with arrays of delta-doped layers is studied theoretically. Two types of the structures are treated. The first type is deterministic, defined by a periodic location of the delta-layers. The second type is stochastic, with a Poissonian location of the delta-layers. In the deterministic case, the r.m.s. deviation $\eta(t)$ of the concentration of the diffusants exhibits an exponential long-time behaviour: $\eta^{\rm det} \sim \exp(-4\pi^2 Dt/a^2)$ where $D > 0$ is the diffusion coefficient and $a > 0$ is the spacing between the delta-layers. In the stochastic case, $\eta(t)$ decreases with a much slower rate: $\eta^{\rm stoch}(t) \sim t^{-1/4}$. A general qualitative (semi-quantitative) discussion is given laying emphasis on stochasticity as a prerequisite of any realistic theory of the diffusional homogenization of sintered materials.

1. Introduction

The diffusional homogenization is a phenomenon manifesting itself as a gradual temporal decrease of the variance of concentration profiles $C(x,t)$ oscillating in space around a mean value $\bar{C}$. In the present paper, for the sake of simplicity, we will consider the diffusional homogenization as a one-dimensional problem. We define $\bar{C}$ as a position-independent quantity. Obviously, if there is no reason for any change of the total number of the diffusants, we may take $\bar{C}$ as a parameter which is constant not only in space but also in time. Thus, the variance

$$\eta^2(t) = \langle [C(x,t) - \bar{C}]^2 \rangle \tag{1}$$

does not depend on x and decreases to zero if $t \to \infty$. If any function $f(x)$ oscillates (either periodically or randomly) around an x-independent value $\bar{f}$, we may define the averaging $\langle\ \rangle$ in the usual sense, assuming the validity of the identity

$$\bar{f} = \langle f(x) \rangle = \lim_{L\to\infty} \frac{1}{L} \int_{-L/2}^{L/2} {\rm d}x\ f(x)\ . \tag{2}$$

The simplest mathematical formulation of the homogenization problem was proposed by Purdy and Kirkaldy [1]. These authors considered a sinusoidal initial concentration profile,

$$C(x,0) \;\equiv\; C_{\sin}(x,0) = \bar{C} + \sqrt{2}\,\eta_0\,\sin(\pi x/l_0)\,. \tag{3}$$

The diffusion equation

$$\frac{\partial C(x,t)}{\partial t} = D\,\frac{\partial^2 C(x,t)}{\partial x^2} \tag{4}$$

is then solvable almost trivially: for $t > 0$, the solution reads

$$C(x,t) \;\equiv\; C_{\sin}(x,t) == \bar{C} + \sqrt{2}\,\eta_{\sin}(t)\,\sin(\pi x/l) \tag{5}$$

with

$$\eta_{\sin}(t) = \eta_0 \exp(-\,\pi^2 Dt/l_0^2)\,. \tag{6}$$

According to this result, the diffusional homogenization is characterized by a relaxation time

$$\tau_{\sin} = \frac{l_0^2}{\pi^2 D} > 0\,. \tag{7}$$

Of course, the sinusoidal concentration profile is too simple to be acceptable for assessing the homogenization rates of processes which are of interest in practice. One of standard metallurgical methods of producing alloys consists in blending constituent powders, compacting them, and subjecting them to high-temperature annealing. When considering powder particles as minute spheres, we have to take into account that their diameters may be scattered to a sizeable extent. This implies that the blend of these particles, when sintered together, has to be regarded as a considerably disordered granular solid. Therefore, as far back as 1972, we proposed (in [2]) to consider the initial concentration $C(x,0)$ as a random function with the (second-order) autocorrelation function

$$W_0^{(a)}(|x_1 - x_2|) = \langle [C(x_1,0) - \bar{C}][C(x_2,0) - \bar{C}] \rangle = \eta_0^2 \exp[-\,(x_1 - x_2)/l_0^2]\,. \tag{8}$$

(The superscript a is to label 'case (a)'; similarly, the superscript b will be used for 'case (b)' corresponding to another autocorrelation function.) With autocorrelation function (8), it was relatively easy to derive the function $\eta(t)$:

$$\eta^{(a)}(t) \;\equiv\; [W_t^{(a)}(0)]^{1/2} = \frac{\eta_0}{[1 + 8Dt/l_0^2]^{3/4}}\,. \tag{9}$$

Although both the functions $\eta_{\sin}(t)$ and $\eta^{(a)}(t)$ tend duly to zero with $t \to \infty$, the decrease of the latter, $\eta^{(a)}(t) \sim t^{-3/4}$, is evidently very slow in comparison with the exponential decrease of $\eta_{\sin}(t)$. As a matter of fact, sintering experiments (as it was pointed out, e.g., in [3]) often disclosed that the homogenization – especially during its final stages – really did not run as quickly as it might have been expected according to the sinusoidal model. This ascertainment points to the necessity of developing the theory of the homogenization kinetics as a stochastic theory.

However, not the stochasticity of $C(x,0)$ as an abstract supposition, but actually the definition of the autocorrelation function of $C(x,0)$ proved to be decisive for the determination of the steepness of the decline of $\eta(t)$ towards zero. Let us point out here that, in contrast to the function $\eta^{(a)}(t)$ falling down less rapidly than the simple exponential, there are also counter-examples showing that the steepness of the decrease of $\eta(t)$ for some stochastic models may even outmatch the steepness of the decrease of the exponential $A\exp(-\,Bt)$ with constant values of $A > 0$ and $B > 0$. Indeed, if we take into account the autocorrelation function

$$W_0^{(b)}(|x_1 - x_2|) = \langle [C(x_1,0) - \bar{C}][C(x_2,0) - \bar{C}] \rangle = \eta_0^2 \exp[-\,|x_1 - x_2|/l_0] \tag{10}$$

$(l_0 > 0)$, we find [4] that

$$\eta^{(b)}(t) \;\equiv\; [W_t^{(b)}(0)]^{1/2} = \eta_0 \left[\mathrm{erfc}\left(\frac{(2Dt)^{1/2}}{l_0}\right)\right]^{1/2}\,. \tag{11}$$

Since $\mathrm{erfc}\,\xi \approx \exp(-\,\xi^2)/(\sqrt{\pi}\xi)$ for large positive values of ξ (cf. [5]), expression (11) implies the asymptotic formula

$$\eta^{(b)}(t) \;\approx\; \eta_0\,\frac{l_0}{\pi^{1/4}(Dt)^{1/2}}\,\exp\left(-\,\frac{Dt}{l_0^2}\right) \quad \text{for} \quad Dt \gg l_0^2$$

and the decrease of this function, when compared to the decrease of the the simple exponential $\exp(-\,Dt/l_0^2)$, is steeper owing to the prefactor $\sim t^{-1/2}$.

The above-mentioned examples clearly suggest that, when considering real exper-
imental samples, our conclusions about the homogenization kinetics drawn from any
simplified model must be rather cautious. Even qualitative predictions may appear to a
certain extent dubious if they are not supported by extensive statistical data obtained
from thorough granulometric investigations of representative sinters. To our best knowl-
edge, there is a general lack of such data. Indeed, even a casual inspection of newest
papers devoted to problems of the powder metallurgy reveals that specialists in the field
still either theorize with particles of some constant radius (then they speak of monosize
ball models, cf. e.g. [6 – 8]) or try to realize only some primary statistical potentialities
of the modelling of the packing of fine particles as a function of particle size and shape
distributions, often in regard to powders before their compaction and almost always on
an empirical level [7, 9]. Further theoretical achievements will probably much depend
on gathering suitable data from automated granulometric techniques enabling particle
size analyses of bulk powders using sophisticated tools of the so-called mathematical
morphology [10]. Nevertheless, even if we admit that there is an appreciable progress
in a general comprehension of how to describe granular materials, we have still to state
that extant results in the statistical characterization of these materials are not sufficient
for elaborating a satisfactory and exhaustive theory yet.

Therefore, as we want to treat the diffusional homogenization as a mathematically well-argued problem, it seems to us at present that it is more justifiable to pay heed to simple models, allowing a clear probabilistic description of which we can have a good grasp, than to formulate complicated models that may have been called for in a realistic theory of sinters. We share this view with Masteller *et al.* [3].

In the present paper we propose to study the homogenization problem for arrays of delta-doped layers embedded in a crystalline material. Such arrays can be studied not only theoretically but also experimentally. The delta-doping is a modern computer-controlled technique [11, 12]. By the delta-doping, it is possible to fabricate semiconductor single crystals in which dopants (donors or acceptors) of a given kind are located in extremely thin layers (delta-layers). We will model the initial perpendicular concentration profile of the dopants in all the delta-layers by a narrow Gaussian of the same height and width. The delta-layers are parallel to each other. Their number n in a sample of length L of some centimetres may be large enough (say about $10^4 - 10^5$) so that when treating the homogenization problem, we may take the sample as 'infinite', neglecting end effects. We assume that if $L \to \infty$, then $n \to \infty$ and

$$\frac{L}{n} \to a \tag{12}$$

where $a > 0$ is a constant. The delta-layers may be distributed at will. If they are distributed equidistantly with some spacing $a > 0$, we speak of the case (a_δ). (This case corresponds to a superlattice). If the delta-doping is programmed in such a way that the result is an array of delta-layers distributed practically at random, in a Poissonian way, with a signifying the mean distance between neighbouring delta-layers, we speak of the case (b_δ). (This case corresponds to a model which may be considered as an analogue of a sinter).

The aim of the present paper is to derive the function $\eta(t)$ for both the cases, (a_δ) and (b_δ). We take the number of the dopants in each delta-layer the same, equal to $N_\delta > 0$. Then, evidently,

$$\bar{C} = \frac{N_\delta}{a} = \frac{N_\delta n}{L} \,. \tag{13}$$

2. Mathematical formulation of the problem

Let x_j be the coordinate of the centre of the jth delta-layer. At the initial time $t_0 = 0$, the concentration profile of the dopants reads

$$C(x,0) = \frac{N_\delta}{(2w_0^2)^{1/2}} \sum_j \exp\left(- \frac{(x - x_j)^2}{2w_0^2} \right) \tag{14}$$

where $w_0 > 0$.

Assuming that $D > 0$ is a well-defined diffusion coefficient of the dopants in the host crystal, we can easily derive the solution of equation (4) at a general time instant $t > 0$:

$$C(x,t) = \frac{N_\delta}{(2\pi)^{1/2}(2Dt + w_0^2)^{1/2}} \sum_j \exp\left(- \frac{(x - x_j)^2}{2(2Dt + w_0^2)} \right) . \tag{15}$$

For the purposes of further calculations, we rewrite expression (15) in the form of the Fourier integral

$$C(x,t) = \frac{N_\delta}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}k \sum_j \exp[\mathrm{i}(x - x_j)k] \, \exp\left[- \left(Dt + \frac{w_0^2}{2} \right) k^2 \right] . \tag{16}$$

We can directly show that $\langle C(x,t) \rangle = \bar{C}$:

$$\langle C(x,t) \rangle = \lim_{L\to\infty} \frac{1}{L} \int_{-L/2}^{L/2} \mathrm{d}x \, C(x,t)$$

$$= \frac{N_\delta}{2\pi} \lim_{L\to\infty} \frac{1}{L} \int_{-\infty}^{\infty} \mathrm{d}k \sum_j \int_{-L/2}^{L/2} \mathrm{d}x \, \exp[\mathrm{i}(x - x_j)k] \, \exp\left[- \left(Dt + \frac{w_0^2}{2} \right) k^2 \right]$$

$$= N_\delta \lim_{L\to\infty} \frac{1}{L} \int_{-\infty}^{\infty} \mathrm{d}k \sum_j \delta(k) = N_\delta \lim_{L\to\infty} \frac{n}{L} = \bar{C} \,. \tag{17}$$

Let us now calculate the averaged function $\langle [C(x,t)]^2 \rangle$. When taking the square of expression (14), we obtain the double sum

$$[C(x,t]^2 = \frac{N_\delta^2}{2\pi(2Dt + w_0^2)} \sum_{j_1,j_2} \exp\left(- \frac{(x - x_{j_1})^2 + (x - x_{j_2})^2}{2(2Dt + w_0^2)} \right)$$

$$= \frac{N_\delta^2}{(4\pi)^{1/2}(2Dt + w_0^2)^{1/2}} \sum_{j_1,j_2} \exp\left(- \frac{(x_{j_1} - x_{j_2})^2}{4(2Dt + w_0^2)} \right)$$

$$\times \frac{1}{\sqrt{\pi}(2Dt + w_0^2)^{1/2}} \exp\left(- \frac{[x - \frac{1}{2}(x_{j_1} + x_{j_2})]^2}{2Dt + w_0^2} \right) . \tag{18}$$

Since

$$\frac{1}{\sqrt{\pi}(2Dt + w_0^2)^{1/2}} \int_{-L/2}^{L/2} \mathrm{d}x \, \exp\left(- \frac{[x - \frac{1}{2}(x_{j_1} + x_{j_2})]^2}{2Dt + w_0^2} \right) \approx 1$$

if L is sufficiently large, we may write the equality

$$\langle [C(x,t]^2 \rangle = \frac{N_\delta^2}{L} \frac{1}{(4\pi)^{1/2}(2Dt + w_0^2)^{1/2}} \sum_{j_1,j_2} \exp\left(- \frac{(x_{j_1} - x_{j_2})^2}{4(2Dt + w_0^2)} \right) . \tag{19}$$

The double summation in formula (19) is self-averaged. The self-averaging (a notion well-known to theorists working in the field of disordered solids) is given by the fact that $L \to \infty$. The number n of the delta-layers may be considered as self-averaged.

3. Mathematical solution of the problem

3.1. Case (a_δ): Periodic array of the delta-layers

In this case,

$$x_j = ja \tag{20}$$

where $j = 0, 1, 2, \dots n-1$. When using the pair of indices $j = j_2 - j_1$, $j' = j_2$ instead of the pair j_1, j_2, we can transform (19) into the double sum

$$\langle [C^{(a_\delta)}(x,t)]^2 \rangle = \frac{N_\delta^2}{L} \frac{1}{(4\pi)^{1/2}(2Dt + w_0^2)^{1/2}} \sum_{j'=0}^{n-1} \sum_{j=j'-n+1}^{n-1} \exp\left(- \frac{a^2 j^2}{4(2Dt + w_0^2)} \right) . \tag{21}$$

Since $n \to \infty$, we may accomplish the summation with respect to j from $-\infty$ to ∞ and so we come to the expression

$$\langle [C^{(a_\delta)}(x,t)]^2 \rangle = \frac{\bar{C}^2 a}{(4\pi)^{1/2}(2Dt + w_0^2)^{1/2}} \left[1 + 2 \sum_{j=1}^{\infty} \exp\left(- \frac{a^2 j^2}{4(2Dt + w_0^2)} \right) \right] : \tag{22}$$

In order to derive the long-time approximation of the sum in formula (22), let us now recall an analogy from the quantum statistical mechanics. Let $C_\beta(\xi, \xi_0)$ be the canonical one-particle density matrix of a one-dimensional system of non-interacting boltzons confined in a box of width π. We assume that ξ, ξ_0 and β are dimensionless variables, $0 < \xi < \pi$, $0 < \xi_0 < \pi$ and $\beta > 0$. The solution of the Bloch equation

$$\frac{\partial C_\beta(\xi, \xi_0)}{\partial \beta} = \frac{\partial^2 C_\beta(\xi, \xi_0)}{\partial \xi^2} \tag{23}$$

with the conditions

$$C_\beta(0, \xi_0) = C_\beta(\pi, \xi_0) = 0 \quad \text{and} \quad C_{+0}(\xi, \xi_0) = \delta(\xi - \xi_0) \tag{24}$$

reads

$$C_\beta(\xi, \xi_0) = \frac{2}{\pi} \sum_{j=1}^{\infty} \exp(-\beta j^2) \sin(\xi_0 j/\pi) \sin(\xi j/\pi) . \tag{25}$$

By applying the Poisson summation formula, we can rewrite (25) (cf. [13]) as an alternative sum:

$$C_\beta(\xi, \xi_0) = \frac{1}{(4\pi\beta)^{1/2}} \left\{ \exp\left(- \frac{(\xi - \xi_0)^2}{4\beta} \right) - \exp\left(- \frac{(\xi + \xi_0)^2}{4\beta} \right) \right.$$
$$+ \sum_{p=1}^{\infty} \left[\exp\left(- \frac{(2\pi p + \xi - \xi_0)^2}{4\beta} \right) + \exp\left(- \frac{(2\pi p - \xi + \xi_0)^2}{4\beta} \right) \right.$$
$$\left. \left. - \exp\left(- \frac{(2\pi p - \xi - \xi_0)^2}{4\beta} \right) - \exp\left(- \frac{(2\pi p + \xi + \xi_0)^2}{4\beta} \right) \right] \right\} . \tag{26}$$

(This sum can also be obtained by employing the method of mirror images.) Hence

$$C_\beta(\xi, \xi) = \frac{1}{(4\pi\beta)^{1/2}} \left\{ 1 - \exp\left(- \frac{\xi^2}{\beta} \right) - \exp\left(- \frac{(\pi - \xi)^2}{\beta} \right) + \sum_{p=1}^{\infty} \left[2 \exp\left(- \frac{\pi^2 p^2}{\beta} \right) \right. \right.$$
$$\left. \left. - \exp\left(- \frac{(\pi p + \xi)^2}{\beta} \right) - \exp\left(- \frac{[\pi(p+1) - \xi]^2}{\beta} \right) \right] \right\} . \tag{27}$$

This expression for $C_\beta(\xi, \xi)$ is especially advantageous if $\beta > 0$ is small. We have to integrate this expression with respect to the variable ξ running from 0 to π:

$$\sum_{j=1}^{\infty} \exp(-\beta j^2) = \int_0^\pi d\xi \, C_\beta(\xi, \xi) . \tag{28}$$

Fortunately,

$$\int_0^\pi d\xi \sum_{p=0}^{\infty} \exp\left(- \frac{(\pi p + \xi)^2}{\beta} \right) = \int_0^\pi d\xi \sum_{p=0}^{\infty} \exp\left(- \frac{[\pi(p+1) - \xi]^2}{\beta} \right)$$
$$= \int_0^\infty d\xi \exp\left(- \frac{\xi^2}{\beta} \right) = \frac{(\pi\beta)^{1/2}}{2} .$$

Therefore,

$$1 + 2 \sum_{j=1}^{\infty} \exp(-\beta j^2) = \left(\frac{\pi}{\beta} \right)^{1/2} \left[1 + 2 \sum_{j=1}^{\infty} \exp\left(- \frac{\pi^2 j^2}{\beta} \right) \right] . \tag{29}$$

After substituting $a^2/[4(2Dt + w_0^2)]$ for β, we can readily write down the formula

$$\langle [C^{(a_\delta)}(x,t)]^2 \rangle = \bar{C}^2 \left\{ 1 + 2 \sum_{j=1}^{\infty} \exp\left[- \frac{4\pi^2 j^2}{a^2} (2Dt + w_0^2) \right] \right\} . \tag{30}$$

In this way we have got the function

$$\eta^{(a_\delta)}(t) = [\langle [C^{(a_\delta)}(x,t)]^2 \rangle - \bar{C}^2]^{1/2}$$
$$= \sqrt{2}\, \bar{C} \left\{ \sum_{j=1}^{\infty} \exp\left[- \frac{4\pi^2 j^2}{a^2} (2Dt + w_0^2) \right] \right\}^{1/2} . \tag{31}$$

(Of course, this result could also be obtained directly, if the periodic function $C(x,t)$ were developed in the cosine Fourier series.) Formulae (30) and (31) are valid exactly for all values of $t \geq 0$. We may also write (31) in the form

$$\eta^{(a_\delta)}(t) =$$

$$\eta_0 \left\{ \sum_{j=1}^{\infty} \exp\left[- \frac{4\pi^2 j^2}{a^2} (2Dt + w_0^2) \right] \right\}^{1/2} \Big/ \left\{ \sum_{j=1}^{\infty} \exp\left[- \frac{4\pi^2 j^2}{a^2} w_0^2 \right] \right\}^{1/2} \quad (32)$$

with

$$\eta_0 \equiv \eta^{(a_\delta)}(0) = \left\{ \sum_{j=1}^{\infty} \exp\left[- \frac{4\pi^2 j^2}{a^2} w_0^2 \right] \right\}^{1/2} . \quad (33)$$

Asymptotically,

$$\eta^{(a_\delta)}(t) \approx \sqrt{2}\, \bar{C} \exp\left(- \frac{2\pi^2 w_0^2}{a^2} \right) \exp\left(- \frac{4\pi^2 Dt}{a^2} \right) \quad \text{for} \quad t \gg \frac{a^2}{4\pi^2 D} \quad (34)$$

Thus, we have derived the following relaxation time for the diffusional homogenization of the delta-periodic model that has been treted here:

$$\tau_{\delta\text{periodic}} = \frac{a^2}{4\pi^2 D} > 0 . \quad (35)$$

3.2. Case (b_δ): Poissonian random array of the delta-layers

When using the representation of $C(x,t)$ by integral (16) and taking into account its square, we are to calculate the expression

$$\langle [C^{(b_\delta)}(x,t)]^2 \rangle =$$

$$\frac{N_\delta^2}{(2\pi)^2} \sum_{j_1,j_2} \int_{-\infty}^{\infty} dk_1 \int_{-\infty}^{\infty} dk_2 \, \frac{1}{L} \int_{-L/2}^{L/2} dx \, \exp\{ i[(x - x_{j_2})k_2 - (x - x_{j_1})k_1] \}$$

$$\times \exp\left[- \left(Dt + \frac{w_0^2}{2} \right) \right] .$$

The first step is to carry out the integration with respect to x:

$$\int_{-L/2}^{L/2} dx \, \exp[i(k_2 - k_1)x] \approx 2\pi\delta(k_2 - k_1) .$$

(The equality symbol $\approx$ means that the equation becomes exact if $L = \infty$. However, we will not strictly distinguish between the symbols $=$ and $\approx$.) Then we obtain the expression

$$\langle [C^{(b_\delta)}(x,t)]^2 \rangle =$$

$$\frac{N_\delta^2}{2\pi L} \sum_{j_1,j_2} \int_{-\infty}^{\infty} dk \, \exp[i(x_{j_2} - x_{j_1})k] \, \exp[-(2Dt + w_0^2)k^2] .$$

This integral has to be calculated separately for $j_1 = j_2$ and for $j_1 \neq j_2$. Owing to the property of the self-averaging, we may write

$$\langle [C^{(b_\delta)}(x,t)]^2 \rangle = \frac{N_\delta^2}{2\pi L} \left\{ n \int_{-\infty}^{\infty} dk \, \exp[-(2Dt + w_0^2)k^2] \right.$$

$$\left. + \, n(n-1) \int_{-\infty}^{\infty} dk \, \langle \exp[i(x_{j_2} - x_{j_1})k] \rangle \exp[-(2Dt + w_0^2)k^2] \right\} . \quad (36)$$

Let us now discuss the second of these integrals. In regard to the Poissonian distribution of the points x_j, we must respect the equality

$$\int_{-\infty}^{\infty} dk \, \langle \exp[i(x_{j_2} - x_{j_1})k] \rangle \exp[-(2Dt + w_0^2)k^2] =$$

$$\frac{1}{L^2} \int_{-\infty}^{\infty} dk \int_{-L/2}^{L/2} dx'' \int_{-L/2}^{L/2} dx' \, \exp[i(x'' - x')k] \, \exp[-(2Dt + w_0^2)k^2] .$$

However,

$$\frac{1}{L} \int_{-\infty}^{\infty} dk \int_{-L/2}^{L/2} dx'' \int_{-L/2}^{L/2} dx' \, \exp[i(x'' - x')k] =$$

$$\frac{1}{L} \int_{-\infty}^{\infty} dk \int_{-L/2}^{L/2} dx \, \exp[ixk] = \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dx \, \exp[ixk] = 2\pi .$$

In this way, we have proved that

$$\left. \frac{N_\delta^2}{2\pi L} n(n-1) \int_{-\infty}^{\infty} dk \, \langle \exp[i(x_{j_2} - x_{j_1})k] \rangle \exp[-(2Dt + w_0^2)k^2] \right\}$$

$$\approx \frac{N_\delta^2 n(n-1)}{L^2} \approx \bar{C}^2 . \quad (37)$$

After putting formulae (36) and (37) together, we obtain the function $[\eta_0^{(b_\delta)}(t)]^2 =$

$$\langle [C^{(a_\delta)}(x,t)]^2 \rangle - \bar{C}^2 = \frac{N_\delta^2}{2\pi} \lim_{L\to\infty} \frac{n}{L} \int_{-\infty}^{\infty} dk \, \exp[-(w_0^2 + 2Dt)k^2]$$

$$= \frac{\bar{C}^2 a}{(4\pi)^{1/2}} \left(\frac{1}{w_0^2 + 2Dt} \right)^{1/2} = \bar{C}^2 \left(\frac{a^2}{8\pi D} \right)^{1/2} \frac{1}{[w_0^2/(2D) + t]^{1/2}} . \quad (38)$$

This result is valid exactly for all values of the time variable $t \geq 0$. For $t = 0$, we obtain the constant

$$\eta_0 = \bar{C} \left(\frac{a^2}{4\pi w_0^2} \right)^{1/4} . \quad (37)$$

Accordingly, we may finally write down the function

$$\eta^{(b_\delta)}(t) = \eta_0 \frac{w_0^{1/2}}{(w_0^2 + 2Dt)^{1/4}} = \bar{C} \left(\frac{a^2}{8\pi D} \right)^{1/4} \frac{1}{[w_0^2/(2D) + t]^{1/4}} . \quad (38)$$

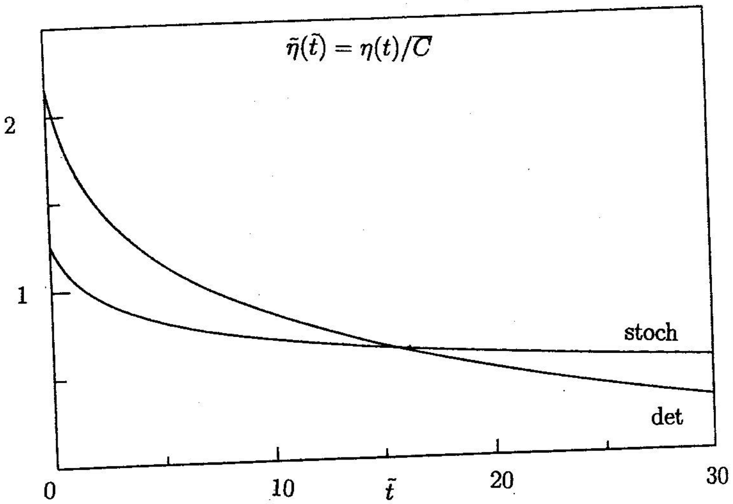

Fig. 1. Plot of the function $\eta(t)/\bar{C}$ (in dimensionless units) for the periodic array (a_δ) and the Poissonian random array (b_δ) of the delta-layers. Both the curves correspond to $\tilde{a} = 20$.

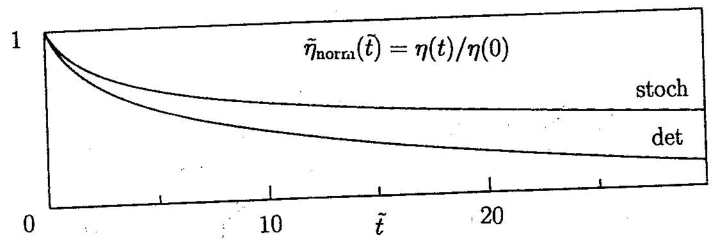

Fig. 2. Plot of the function $\eta(t)/\eta(0)$ (in dimensionless units) for the periodic array (a_δ) and the Poissonian random array (b_δ) of the delta-layers with the same value of the parameter $\tilde{a}$ as in Fig. 1: $\tilde{a} = 20$.

4. Graphical presentation of results

To draw a graphical presentation of the functions $\eta^{\rm det}(t)$ and $\eta^{\rm stoch}(t)$, it is suitable to use dimensionless variables. We take w_0 (the parameter characterizing the half-width of the Gaussians at the initial time $t_0 = 0$) as the length unit; then the dimensionless parameter

$$\tilde{a} = \frac{a}{w_0} \tag{39}$$

plays the role of the parameter a. Employing $w_0^2/(2D)$ as the time unit, we introduce the dimensionless variable

$$\tilde{t} = \frac{2Dt}{w_0^2} \tag{40}$$

playing the role of the time variable. Then it is advisable to plot either the functions

$$\tilde{\eta}^{\rm \ det}(\tilde{t}) = \frac{\eta^{(a_\delta)}(t)}{\bar{C}} , \quad \tilde{\eta}^{\rm \ stoch}(\tilde{t}) = \frac{\eta^{(b_\delta)}(t)}{\bar{C}} , \tag{41}$$

or the normalized functions

$$\tilde{\eta}_{\rm norm}^{\rm det}(\tilde{t}) = \frac{\eta^{(a_\delta)}(t)}{\eta_0} , \quad \tilde{\eta}_{\rm norm}^{\rm stoch}(\tilde{t}) = \frac{\eta^{(b_\delta)}(t)}{\eta_0} , \tag{42}$$

$$\tilde{\eta}_{\rm norm}^{\rm det}(0) = \tilde{\eta}_{\rm norm}^{\rm stoch}(0) = 1 . \tag{43}$$

Note that $\tilde{a}$ is the only parameter present in these functions.

Then, from formulae (22) and (31), we obtain the function

$$\tilde{\eta}^{\rm \ det}(\tilde{t}) = \left\{ \frac{1}{(4\pi)^{1/2}} \frac{\tilde{a}}{(\tilde{t}+1)^{1/2}} \left[1 + \sum_{j=1}^{\infty} \exp\left(- \frac{\tilde{a}^2 j^2}{4(\tilde{t}+1)} \right) \right] - 1 \right\}^{1/2}$$
$$= \sqrt{2} \left\{ \sum_{j=1}^{\infty} \exp\left[- \frac{4\pi^2 j^2}{\tilde{a}^2} (\tilde{t}+1) \right] \right\}^{1/2} . \tag{44}$$

Similarly, expression (38) is transformed into the function

$$\tilde{\eta}^{\rm \ stoch}(\tilde{t}) = \frac{1}{(4\pi)^{1/4}} \frac{\tilde{a}^{1/2}}{(\tilde{t}+1)^{1/4}} . \tag{45}$$

Fig. 1 shows the functions $\tilde{\eta}^{\rm \ det}(\tilde{t})$ and $\tilde{\eta}^{\rm \ stoch}(\tilde{t})$ calculated for $\tilde{a} = 20$.

For the functions $\tilde{\eta}_{\rm norm}^{\rm det}(\tilde{t})$ and $\tilde{\eta}_{\rm norm}^{\rm stoch}(\tilde{t})$, we have got the expressions $\tilde{\eta}_{\rm norm}^{\rm det}(\tilde{t}) =$

$$\left\{ \sum_{j=1}^{\infty} \exp\left[- \frac{4\pi^2 j^2}{\tilde{a}^2} (\tilde{t}+1) \right] \right\}^{1/2} \Big/ \left\{ \sum_{j=1}^{\infty} \exp\left[- \frac{4\pi^2 j^2}{\tilde{a}^2} \right] \right\}^{1/2} \tag{46}$$

and

$$\tilde{\eta}_{\rm norm}^{\rm stoch}(\tilde{t}) = \frac{1}{(\tilde{t}+1)^{1/4}} . \tag{47}$$

These two functions are depicted in Fig. 2 (again for $\tilde{a} = 20$).

5. Conclusion

The purpose of this paper was to present a theory of the diffusional homogenization of samples with identical delta-layers. When considering each delta-layer as a source of N_δ diffusants, we may take the concentration $C(x,t)$ of the diffusants as a sum of equal Gaussians at any time instant $t > 0$. Our aim was to calculate the r.m.s. deviation $\eta(t)$ of $C(x,t)$ in two typical cases which we called case (a_δ) and case (b_δ). The case (a_δ) (cf. subsections 2.1 and 3.1) denoted a deterministic situation where the set of the delta-layers was chosen as an equidistant array with some spacing a. The case (b_δ) (cf. subsections 2.2 and 3.2) denoted a stochastic situation with a Poissonian distribution of the delta-layers. In the latter case, a was defined as the mean distance between neighbouring layers.

In the deterministic case, we have derived the function $\eta^{\mathrm{det}}(t) \equiv \eta^{(a_\delta)}(t)$ in the form of an infinite series and proved its reduction to a single exponential function (cf. formula (34)) in the long-time approximation. In the stochastic case, we have ascertained, in concordance with what we had concluded long ago in [2] with another model, that the randomization of the initial concentration profile brings about a remarkable decelerating effect upon the diffusional homogenization. Indeed, the function $\eta^{\mathrm{stoch}}(t)$ that we have derived in the case (b_δ) (cf. formula (38)) decreases to zero very slowly in comparison with the exponential decrease predicted for $\eta(t)$ in the periodic case (a_δ).

A natural question arises if the calculations that we have presented here with the intentional restriction to one-dimensional models can be repeated with analogical three-dimensional models. Our answer is positive. Calculations in this sense should deserve a special attention in an independent paper.

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