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The phase transition for the aggregation model in the effective-medium approach

M G Rudavets

Laboratory of Mathematical Physics, Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 142432, Moscow Region, Russia

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Abstract. The one-particle model on a lattice is proposed to account for the formation of a spanning cluster in the aggregation process. In the framework of that model, effective-medium theory is described to calculate the effective diffusion rate, $\bar{\sigma}$, and effective adsorption rate, $\bar{\nu}$, within the aggregation front. A sharp increase in $\bar{\nu}$ is found at a very small concentration of adsorbed particles if the elementary rate of attachment, Γ , measured in units of the elementary diffusion rate, is above a critical value $\Gamma^* \simeq 2$. This peculiarity in behaviour of $\bar{\nu}$ signals the occurrence of rare and ramified structure. The model can also be applied to explore the concentration dependence of adsorption rate. A unit rate of attachment, Γ , corresponds to instantaneous local absorption. Then, the Smoluchowski result is reproduced for a small concentration of traps. Values $\Gamma < 1$ account for the reaction-limited mode. The concentration dependences of the rates $\bar{\nu}$ and $\bar{\sigma}$ are found for any value Γ in the steady-state regime.

1. Introduction

In the conventional theory of diffusion-limited processes [1], diffusion-limited aggregation (DLA) is considered to be the result of the free diffusion of particles, say A, from a spatially uniform solution to a flat interface, solution/solid deposit of B, at which a constant concentration $n_a = 0$ is maintained, followed by instant attachment of diffused particles to the interface. Once a distribution n_a is found, the motion of the interface, $x_b(t)$, can be determined from the conservation law for particle number in the conversion process $A \rightarrow B$, asserting that the flows of particles coming from the liquid phase to the solid phase per unit time are equal, i.e.

$$n_b^* dx_b(t)/dt = d_a \nabla n_a(x_b, t)$$

where d_a is the diffusion coefficient of A particles and n_b^* is the effective concentration of the deposit.

A new situation arises if initially the system contains no A particles and some source generates a small flow of A particles to the substrate surface, where deposition and the growth of the aggregate take place. Such processes are currently investigated with stochastic rules; the fractal structure of the adsorbed particles is revealed here, showing that the interface is far from being flat [2, 3]. Its roughness, ξ , is proportional to the linear size of the aggregate l , i.e. $\xi \simeq l$, which is itself connected with the total number of adsorbed particles N_b by the power-law relationship $l \simeq N_b^{1/D_f}$, where D_f is the fractal dimension [2, 3].

An objective of this paper is to explore transport coefficients within the adsorption front by considering its structure as an effective medium, disregarding large-scale fluctuation effects. At first sight, the shielding effect of inner regions of deposited film appears when the effective diffusion terminates. Indeed, if we substitute $d_a(x) = 0$ into the expression for the distribution of A particles

$$n_a(x, t) = n_a^0 \operatorname{erfc} \left\{ x / [4d_a(x)t]^{1/2} \right\} \quad (1)$$

which possesses the required properties (namely, at $t = 0$ concentration $n_a(x, t = 0) = 0$ overall in the volume, and $n(0, t) = n_a^0$ at the source placed at $x = 0$), then the concentration at point x will satisfy the condition $n_a(x, t) = 0$ characteristic for the interface. However, this reason for shielding appears not to be the case. From [2, 3], the aggregate's concentration vanishes as $n_b \simeq l^{D_t - D} \rightarrow 0$ at $l \rightarrow \infty$, where D is the Euclidean dimension. At such small concentrations of ill-conducting places, the effective diffusion coefficient practically coincides with the diffusion coefficient in a free system. Thus, the formation of the B structure that totally screens its own inner regions from incoming flow implies the occurrence of a large adsorption coefficient of A particles, while their penetration is ideal.

In this paper, we present a model that provides a sharp increase in effective adsorption rate at a very small concentration of adsorbent structure of B kind. These properties are common for ramified and rare clusters constructed with stochastic rules [2, 3]. The many-body Liouvillean of the system, L , is introduced in section 2. Since it is futile to expect its exact solution, an approximate Liouvillean (alloy Liouvillean, due to terminology in the Hubbard model) and, corresponding to it, one-particle kinetics equations with random rates are derived. In section 3, the one-particle model is extended to a more general one, permitting one to explain the process of deposition as critical phenomena. The effective-medium theory applied to calculations of adsorption and diffusion rates in the deposition front is described in section 4. This is followed by analytical results for the low-concentration case, $n_b \rightarrow 0$; in particular, the Smoluchowski rate constant is reproduced here. For arbitrary concentration n_b , solution of the self-consistent equations of the effective-medium theory have been found numerically, including the critical concentration of the effective structure n_b^* to be discussed in section 5. Finally, the conclusions are summarized in section 6.

2. Liouvillean of the diffusion-limited aggregation

The many-body process of aggregation of A particles on a lattice is described with the Liouvillean L [4], consisting of diffusion, L_D , and reaction, L_R , parts

$$L = L_D + L_R$$

with

$$\begin{aligned} L_D &= d_a \sum_{j,e} (1 - \hat{n}_{b,j+e}) (a_{j+e}^{\dagger} - a_j^{\dagger}) a_j \\ L_R &= d_a \sum_{j,e} \hat{n}_{b,j+e} (b_j^{\dagger} - a_j^{\dagger}) a_j. \end{aligned} \quad (2)$$

Here $a_j, (a_j^\dagger), b_j, (b_j^\dagger)$ are Pauli operators for A and B particles, respectively, with properties

$$[a_j, a_j^\dagger]_+ = 1 \quad a_j^2 = 0 \quad (a_j^\dagger)^2 = 0 \quad [a_i, a_j^\dagger] = 0 \quad \text{for } i \neq j$$

and $\hat{n}_{b,j}$ is the occupation number operator for particles of B in the j th cell. Here L_D corresponds to hops of an A particle from the j th cell to a neighbouring cell ($j + e$) containing no B particle, i.e. $n_{b,j+e} = 0$; while L_R describes the destruction of an A particle in the j th cell with rate d_a and the simultaneous creation in its place of a particle of B when $n_{b,j+e} = 1$. This term implies an instantaneous local annihilation reaction, so the net rate of transition is controlled by the rate of hops of reactant A to the adjacent cell occupied by a B particle. The scheme of the reaction can be followed by using two channels of the transitions in Fock vector space $\{|a_r\rangle, |b_r\rangle\}$

$$|a, j\rangle |b, j + e\rangle \xrightarrow{d_a} |b, j\rangle |b, j + e\rangle \tag{3a}$$

$$|a, j\rangle |0, j + e\rangle \xrightarrow{d_a} |0, j\rangle |a, j + e\rangle. \tag{3b}$$

To get around the many-body problem, we take advantage of the Hubbard model analogy [5, 6], and describe the original problem approximately with the help of a linearized Liouvillean, in which the occupation number operators $\hat{n}_{b,j}$ are replaced with 'c-numbers' $\theta_{b,j}$ ($= 0, 1$). As a result of the simplification, one-particle probabilities (volume fractions) $n_{\rho,j}(t)$ in the total state vector

$$|n(t)\rangle = \sum_{\rho,j} n_{\rho,j}(t) |\rho, j\rangle \quad \rho = a, b \tag{4}$$

solve a linear kinetic equation

$$\partial_t n_{a,j} = d_a \delta_{b,j} \sum_e n_{a,j+e} - d_a n_{a,j} \sum_e \delta_{b,j+e} - d_a n_{a,j} \sum_e \theta_{b,j+e} \tag{5a}$$

$$\partial_t n_{b,j} = d_a n_{a,j} \sum_e \theta_{b,j+e} \tag{5b}$$

where $\delta_{b,j} = 1 - \theta_{b,j}$. The first two terms in equation (5a) correspond to the Lorentz model for diffusion on a restricted lattice [7], and the third term describes reaction (3a). The step functions $\delta_{b,j}$ and $\theta_{b,j}$ allow us to distinguish the channels of diffusion and reaction. In the following, the $\theta_{b,j}$ function is supposed to be determined statistically, with distribution function f being instantaneously adjusted to the elapsed effective concentration of the solid phase of B, $c_{b,i} = \langle n_{b,i}(t) \rangle$, i.e.

$$f(\theta_{b,i}, t) = c_{b,i} \delta(\theta_{b,i} - 1) + (1 - c_{b,i}) \delta(\theta_{b,i}). \tag{6}$$

Given quantity $c_{b,i}$, equation (5a) yields a self-contained description of the kinetics. As stressed above, equation (5a) is equivalent to an equation describing instant local absorption of A particles,

$$\partial_t n_{a,j} = d_a \Delta n_{a,j} - U n_{a,j} \theta_{b,j} \quad \text{where } U \rightarrow \infty. \tag{7}$$

This is due to the fact that both equations describe the free diffusion on a part of the lattice containing no B particles (there $\theta_{b,j} = 0$), and describe the absence of A particles on cells occupied with B particles ($\theta_{b,j} = 1$). Thus, equation (7) as well as equation (5a) supplemented with statistics (6) is not capable of describing interface motion, as its location $r(t)$ is at motionless cells with $n_{a,r}(t) = 0$. The message of this exercise is that, although the many-body Liouvillean (2) accounts for the effect of displacement of individual particles of B in elementary processes of diffusion and reaction, its linearized approximation based on one-particle equations (5) and (6) loses that important property. It is evident rather generally that, to arrive at any useful result, some sort of linearization for L should be implemented. In the next section, we shall show that it is possible to adapt the Liouvillean (2) by increasing the reaction term L_R by a factor of Γ without changing L_D . The linearized approximation of the new Liouvillean accounts for the effect of formation of the new structure.

3. One-particle model of aggregation

To alleviate the problem, we drop out index a in equation (5a) and rewrite it in somewhat more general form by introducing a factor Γ for the rate of the reaction,

$$\partial_t n_r = \sum_c \sigma_{r,r+c} (n_{r+c} - n_r) - \Gamma n_r \sum_c \theta_{r+c} \quad (8)$$

with all rates measured in units of d_a . The relation satisfied by diffusion rates $\sigma_{r,r'}$ between nearest-neighbour cells r and r' can be written as $\sigma_{r,r'} = \delta_{b,r'} \delta_{b,r}$. It is consistent with equation (5a) since an entrance of A particles to the r th cell occurs only from those adjacent cells r' in which the B particles are absent, i.e. $n_{b,r'} = 0$, and hence $\delta_{b,r'} = 1$. The expression for $\sigma_{r,r'}$ is also consistent with separation of the total process into two different pathways: reaction and diffusion. For an available bond state, $\sigma_{r,r'} = 1$, the cell r into which an A particle hops does not contain the B particle, i.e. $\delta_{b,r} = 1$, and for a broken bond, where $\sigma_{r,r'} = 0$, we have $\delta_{b,r} = 0$.

The value of parameter Γ is very important for further considerations. By increasing Γ , we go from one scenario of the kinetics to the other. Thus $\Gamma = 0$ is responsible for diffusion without adsorption, when the particles of A are reflected from ill-conducting regions of the B phase. Values $0 \leq \Gamma \leq 1$ model a local reaction-limited absorption. In this case, the two-cell recombination rate can be represented in the form $\Gamma = U/(1 + U)$, where U is the local (one-cell) rate of the reaction measured in units d_a . The model with $\Gamma = 1$ describes instantaneous local absorption, i.e. $U = \infty$. Renormalization of the local rate has been performed in this case and non-local diffusion with rate d_a governs the kinetics of the destruction of the A particles (see equation (5a)). Values $\Gamma > 1$ model sticking of an A particle to a B cluster if the particle of A is at the border of the cluster. It is worth calling attention to the analogy with similar formulae that have been derived for $\Gamma < 1$ or $U \leq \infty$. In the latter case, the non-locality in the reaction term is simply caused by the mathematical fact of renormalization of the large rate U , the effective rate of absorption being diffusion-controlled. The former case, i.e. $\Gamma > 1$, imitates the growth process, providing a new physical situation. For Γ not deviating by much from unity, the sticking process is slow, while $\Gamma \gg 1$ models instant sticking. Actually, for $\Gamma \gg 1$, it is possible to carry out renormalization in equation (8) and to obtain a

reaction rate with larger non-locality. However, having in mind an application of the effective-medium theory with the smallest cluster size, the present form, i.e. equation (8), is supposed to be more favourable than the renormalized one. We close this section by simply noting that equation (8) is deduced from a linear approximation to the Liouvillean (2) with reaction term ΓL_R .

4. Transport coefficients in an effective medium

4.1. Introduction

The failure of the exact solution to equation (8) with random rate coefficients gives rise to the necessity to get an approximate solution with coefficients averaged over some region of the lattice. To this end, the effective-medium theory (EMT) for calculating the diffusion rates on a lattice with random bonds or sites can be employed [6, 8]. The EMT is known to be rather representative if a $30 \times 30 \times 30$ lattice is used. Numerically calculated effective diffusion on that small lattice appears in qualitative agreement with the analytical result for effective mobility for an infinite lattice. This fact is of importance for application of the EMT to a spatially heterogeneous medium as it indicates that diffusion coefficients calculated analytically for the infinite lattice can be attributed to local values for diffusion rates if a small lattice consisting of about 1000 cells is thought of as a unit of volume.

With respect to transport in a stochastic medium, of much literature published, [7–10] are noteworthy. Comparison of the diagrammatic analysis of diffusion rate in the Lorentz model without reaction [7], numerical simulations and effective-medium results [8–10] show a good agreement of these tools for description of the effective properties at high concentrations of the components. As the EMT has more transparent form than the diagrammatic treatment, it suggests that it is reasonable to apply the cluster scheme of the EMT to the present model, which incorporates chemical reactions as well. Moreover, relying on the EMT, we shall uphold the phenomenological point of view, rather than the mathematically more rigorous formalism of the cluster T -matrix [12].

4.2. Dyson equation for the model

In the Green function (GF) formalism [13] in the Laplace transform domain, the GF P_r corresponding to equation (8) for an A particle starting out from arbitrary cell R reads

$$\omega P_r = \delta_{r,R} + \sum_e \sigma_{r,r+e} (P_{r+e} - P_r) - \Gamma P_r \sum_e \theta_{r+e} \tag{9}$$

where $(r+e)$ is adjacent to cell r and the explicit dependence of P_r on R is dropped, leaving only the dependence on r , i.e. $P_r \equiv P_{r,R}$. The GF with coefficients $\bar{\sigma}$ and $\bar{\nu}$ for the effective lattice fulfils the equation

$$\omega P_r^0 = \delta_{r,R} + \bar{\sigma} \sum_e (P_{r+e}^0 - P_r^0) - \bar{\nu} P_r^0. \tag{10}$$

Taking P_r^0 as an undisturbed solution to equation (9), we can write the Dyson equation in the form

$$P_r = P_r^0 + \sum_{(s,r')} G_{r,s}^0 \{ \Delta_{s,r'} (P_{r'} - P_s) - \xi_{r'} P_s \} \tag{11}$$

where $G_{r,s}^0$ is the GF for transition from the s th to the r th cell on the effective lattice and $\langle s, r' \rangle$ refer to neighbouring cells, $r' = s + e$. For convenience, we use throughout the paper two different notations for the GF on the effective lattice, i.e. P_r^0 and $G_{r,r'}^0$, with the relation $P_r^0 = G_{r,R}^0$ holding. The quantities $\Delta_{r,r'}$ and ξ_r measure fluctuations of diffusion rate of the bond $(r-r')$ and adsorption rate on cell r relative to its effective values, respectively, i.e.

$$\Delta_{r,r'} = \sigma_{r,r'} - \bar{\sigma} \quad (12a)$$

$$\xi_r = \Gamma\theta_r - \bar{v}. \quad (12b)$$

To state self-consistent equations for $\bar{\sigma}$ and \bar{v} , we choose the effective GF P_r^0 as satisfying Bruggeman's condition $P_r^0 = \langle P_r \rangle$ [14], where the averaging is carried out over statistics (6). It follows that both equations (9) and (10) are equivalent if bilinear combinations in equation (9) are represented, on average, as

$$\langle \sigma_{r,r'}(P_{r'} - P_r) \rangle = \bar{\sigma} \langle P_{r'} - P_r \rangle \quad (13a)$$

$$\Gamma \langle P_r \theta_{r+e} \rangle = \bar{v} \langle P_r \rangle. \quad (13b)$$

In other words, the fluctuating variables are considered as if they were statistically independent. In terms of the fluctuations ξ_r and $\Delta_{r,r'}$, equations (13) become

$$\langle \Delta_{r,r'}(P_{r'} - P_r) \rangle = 0 \quad (14a)$$

$$\langle P_r \xi_{r+e} \rangle = 0. \quad (14b)$$

4.3. Solution of the Dyson equation on a finite cluster

An exact calculation of equation (11) is just a bit more difficult than the solution of the corresponding equation (9). A decisive benefit of the EMT is in choosing a cluster embedded into the effective lattice [10]. The solution to equation (11) simplifies when considering a symmetric coherent cluster with side twice the side length of the lattice (see figure 1). All bonds in that cluster are correlated, having the same diffusion rate σ . More precisely, if the central cell has $\delta_{b,i} = 0$, then all six bonds with common cell i have $\sigma_{i,j} = 0$. Spherically symmetric and homogeneous inclusion in the continuum effective medium [15] can be thought of as a continuum analogue of the corresponding lattice. Except for the mentioned correlations between bonds that are caused solely by geometric character, there is correlation between the processes of destruction and hops of A particles within the cluster. This correlation has the same origin as in the model (5a), permitting the particle to follow one of the two channels, either diffusion or adsorption depending on the value of θ_0 . As a result, the fluctuations in ξ_r and $\Delta_{r,r'}$ take the form: (i) $\Delta_{r,r'} = \Delta_0 = \sigma - \bar{\sigma}$, if both r and $r' \in \mathbb{C}$; (ii) $\Delta_{r,r'} = 0$, if at least r or $r' \notin \mathbb{C}$; besides $\sigma = 1 - \theta_0$. Analogously, (iii) $\xi_r \equiv \xi_0 = \Gamma\theta_0 - \bar{v}$, if $r \in \mathbb{C}$; (iv) $\xi_r = 0$, if $r \notin \mathbb{C}$.

To find the probability for formation of the coherent cluster \mathbb{C} , we make use of its definition: all cells in the cluster have no B particles if at least two cells of any six bonds (O-E $_{\alpha}$) (where $\alpha = 1, 2, \dots, 6$) contain no B particles. That state occurs randomly with probability p^2 , where $p = 1 - c_b$, and then $\sigma = 1$. The probability $1 - p^2$ corresponds to a filled cluster with B particles, and hence $\sigma = 0$.

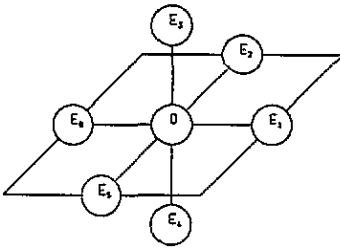


Figure 1. Symmetric cluster, C, in a three-dimensional simple cubic lattice. All bonds (O-E_i) of the cluster have the same diffusion rate of A particles, σ , either 1 or 0. In the former case, the seven cells are empty; and in the latter case, they are filled with B particles.

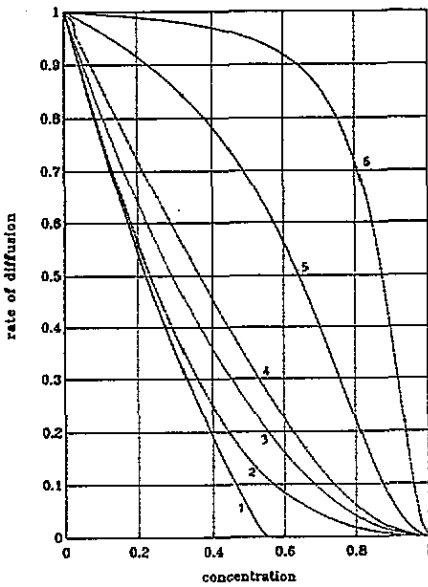


Figure 2. The diffusion rate of A particles, $\bar{\sigma}$, versus the concentration of solid phase of B for different values of the rate of attachment Γ : (1) 0, (2) 0.1, (3) 1, (4) 10, (5) 100, (6) 1000. The curve with $\Gamma = 0$ corresponds to the three-dimensional result of [10] for the percolation problem.

Having defined values ξ_r and $\Delta_{r,r'}$ on the lattice, equation (11) simplifies to

$$P_r = P_r^0 + \Delta_0 \sum_{\alpha=1}^6 (G_{r,0}^0 - G_{r,\alpha}^0) (P_\alpha - P_0) - \xi_0 \sum_{\alpha=1}^6 G_{r,\alpha}^0 P_\alpha - 6\xi_0 G_{r,0}^0 P_0. \tag{15}$$

Owing to equation (15) the GF P_r for every cell r is expressed via the GF of the cluster, i.e. P_0 and $P_\alpha \equiv P_{e_\alpha}$, where $\alpha = 1, \dots, 6$. The $G_{r,\alpha}^0 \equiv G_{r,e_\alpha}^0$ for the simple cubic lattice fulfil the equality $G_{r,\alpha}^0 = G_{\alpha,r}^0$. The symmetry inherent in equation (15) allows it to be solved by putting into equation (15) $r = 0$ and $r = e_\beta$, $\beta = 1, \dots, 6$. First, we introduce shorthand notations for combinations of GF

$$m_0 = 1 + 6\xi_0 G_{00}^0 + 6\Delta_0 (G_{00}^0 - G_{01}^0) \tag{16a}$$

$$m_1 = 6\xi_0 G_{01}^0 + \Delta_0(6G_{01}^0 - g^0) \quad (16b)$$

$$m_2 = \Delta_0(G_{00}^0 - G_{01}^0) - \xi_0 G_{01}^0 \quad (16c)$$

$$m_3 = 1 - 6\Delta_0 G_{01}^0 + (\Delta_0 + \xi_0)g^0 \quad (16d)$$

where

$$g^0 = \sum_{\alpha=1}^6 G_{e_1, e_\alpha}^0.$$

These variables arise as factors in front of GF P_r in equation (15). Then, the GF for the central cell, $r = 0$, reads

$$P_0 = m_0^{-1}(P_0^0 + m_2 S) \quad S = \sum_{\alpha=1}^6 P_\alpha. \quad (17)$$

To determine the value of S , one needs to find g^0 . Owing to the symmetry of the GF, g^0 can be represented as

$$g^0 = \sum_{\alpha=1}^6 G_{e_\alpha, e_1}^0.$$

Then, by putting into equation (10) $r = 0$ and $R = e_1$, we get in explicit form

$$\omega G_{0, e_1}^0 = \bar{\sigma} \sum_{\alpha=1}^6 (G_{e_\alpha, e_1}^0 - G_{0, e_1}^0) - 6\bar{v} G_{0, e_1}^0,$$

so g^0 satisfies the relationship

$$\bar{\sigma} g^0 = (\omega + 6\bar{\sigma} + 6\bar{v}) G_{01}^0. \quad (18)$$

For a neighbouring cell, we have from equation (15)

$$P_\beta = P_\beta^0 - m_1 P_0 + \sum_{\alpha=1}^6 [(G_{01}^0 - G_{\beta, \alpha}^0) \Delta_0 - \xi_0 G_{\beta, \alpha}^0] P_\alpha \quad \beta = 1, \dots, 6 \quad (19)$$

and it follows that

$$S = m_3^{-1}(S^0 - 6m_1 P_0) \quad S^0 = \sum_{\alpha=1}^6 P_\alpha^0. \quad (20)$$

Overall in equations (16)–(20), the symmetry of GF $G_{\alpha, \beta}^0$ on a simple cubic lattice has been used. Equations (17) and (20) have a solution expressed via the GF of the effective lattice

$$\begin{aligned} P_0 &= M^{-1}(m_3 P_0^0 + m_2 S^0) \\ S &= M^{-1}(m_0 S^0 - 6m_1 P_0^0) \end{aligned} \quad (21)$$

where

$$M = m_0 m_3 + 6m_1 m_2. \quad (22)$$

Moreover, as the values S^0 and P_0^0 belong to the effective lattice, they are related to each other by equation (10) (by putting into it $r = 0$ and $R \neq 0$), namely

$$\bar{\sigma} S^0 = (\omega + 6\bar{\sigma} + 6\bar{v}) P_0^0. \quad (23)$$

4.4. Explicit form for the self-consistent equation for $\bar{\sigma}$

Having obtained the cells' GF via effective ones, we then go on to derive an explicit form for the self-consistent equations. To do this requires an elimination of P_0 from equations (17) and (19), with the result

$$P_\beta = A_\beta^0 + \sum_{\alpha=1}^6 h_{\beta\alpha} P_\alpha \quad \beta = 1, \dots, 6 \quad (24)$$

where the constants $A_\beta^0 = P_\beta^0 - m_0^{-1} m_1 P_0^0$, and matrix $h_{\beta\alpha}$ has components

$$h_{\beta\alpha} = \Delta_0(G_{10}^0 - G_{\beta,\alpha}^0) - \xi_0 G_{\beta,\alpha}^0 - m_1 m_2 m_0^{-1}.$$

Now we can write a self-consistent equation on a coherent cluster for two successive bonds (e_6 -O) and (O- e_1) with common cell $r = 0$

$$\langle \Delta_0(P_\alpha - P_0) \rangle = 0 \quad \alpha = 1, 6 \quad (25)$$

and then take their combination

$$\langle \Delta_0(P_1 - P_6) \rangle = 0. \quad (26)$$

An expression for $(P_1 - P_6)$ follows from equation (24), giving

$$P_1 - P_6 = (P_1^0 - P_6^0) / [1 + (\Delta_0 + \xi_0)(G_{00}^0 - G_{16}^0)]. \quad (27)$$

If there is no reaction, i.e. $\Gamma = 0$ and hence $\xi_0 = 0$, then equation (25) is consistent with the equation of Bernasconi and Wiesmann [10]

$$\langle P_1 - P_6 \rangle = P_1^0 - P_6^0. \quad (28)$$

The latter equation has a physical interpretation in terms of the conductivity of the lattice, asserting that the potential drop between cells e_1 and e_6 in the effective lattice is equal to the potential drop averaged over the values σ of the coherent inclusion in the non-homogeneous lattice. In general, except for the condition for a flow through the cluster (see equation (26)), one can construct a condition for the total flow towards the central cell at $r = 0$ from all six neighbouring cells, i.e.

$$\langle \Delta_0(6P_0 - S) \rangle = 0. \quad (29)$$

However, equation (29) yields a poor behaviour for $\bar{\sigma}$ when applied to the case $\Gamma \rightarrow 0$. It should be emphasized that for $\Gamma > 0$ equations (26) and (27) represent a correct condition for $\bar{\sigma}$, but equation (28) does not, as would seem to be so from the above interpretation.

We therefore arrive at a self-consistent equation for $\bar{\sigma}$:

$$\frac{p^2(1 - \bar{\sigma})}{1 + (1 - \bar{\sigma} - \bar{v})(G_{00}^0 - G_{16}^0)} - \frac{(1 - p^2)\bar{\sigma}}{1 + (\Gamma - \bar{\sigma} - \bar{v})(G_{00}^0 - G_{16}^0)} = 0. \quad (30)$$

As for its properties, the following ones can be immediately stated. First, if $c_b \rightarrow 0$, i.e. $p \rightarrow 1$, equation (30) yields $\bar{\sigma} \rightarrow 1$ for every value of Γ . Secondly, if $\Gamma = 0$, then $\bar{v} = 0$ (this equality will be proved in section 4.5) and equation (30) coincides with the self-consistent equation (28). Thirdly, if $\Gamma = 1$ then the denominators in both terms in equation (30) are equal and

$$\bar{\sigma} = p^2 \quad (31)$$

solves equation (30). Fourthly, if $\Gamma \gg 1$ then $\bar{\sigma} = 1$ represents a solution to equation (31). For other values of Γ , numerical analysis of equation (30) together with a self-consistent equation for \bar{v} is amenable to find $\bar{\sigma}$.

4.5. Explicit form for the self-consistent equation for \bar{v}

To calculate \bar{v} , we make use of equation (14b) and take a linear combination of $\langle \xi_0 P_0 \rangle$ and $\langle \xi_0 S \rangle$ in such a manner as to provide the Smoluchowski kinetics for $\bar{v}(c_b)$ in the limit as $c_b \rightarrow 0$. To this end, we impose the following condition:

$$\langle \xi_0(6P_0 + S) \rangle = 0. \quad (32)$$

Hence, a self-consistent equation for \bar{v} is obtained by substituting into equation (32) the expressions for P_0 and S from equation (21), so

$$\left\langle \xi_0 \frac{(\omega/6 + \bar{\sigma} + \bar{v})\bar{\sigma}^{-1}(m_0 + 6m_2) - m_1 + m_3}{M} \right\rangle = 0. \quad (33)$$

In accordance with the choice of the coherent cluster, the averaging in equation (33) encompasses two configurations of the Poisson distribution. With probability p^2 configuration A is realized, for which

$$\begin{array}{ll} \sigma = 1 & \text{i.e.} \quad \Delta_0 = 1 - \bar{\sigma} \\ \theta_0 = 0 & \xi_0 = -\bar{v} \end{array} \quad (34a)$$

and with probability $(1 - p^2)$ configuration B is formed, for which

$$\begin{array}{ll} \sigma = 0 & \text{i.e.} \quad \Delta_0 = -\bar{\sigma} \\ \theta_0 = 1 & \xi_0 = \Gamma - \bar{v}. \end{array} \quad (34b)$$

We restrict our analysis only to the static case, when $\omega = 0$. Regardless as to how $\{m_i\}$ are chosen, equation (33) shows that $\bar{v} = 0$ is its solution when $\Gamma = 0$. Now, consider the case with local instantaneous reaction, $\Gamma = 1$, and a low concentration of solid phase of B, $c_b \rightarrow 0$. A slow adsorption of the A particles is expected to occur in those conditions. The property $\bar{v} \rightarrow 0$ as well as $\bar{\sigma} \rightarrow 1$ results in a chief contribution to coefficients $\{m_i\}$ in equation (16). For configuration A, we have $m_0 \rightarrow 1$, $m_1 \rightarrow 0$, $m_2 \rightarrow 0$, $m_3 \rightarrow 1$, and the corresponding contribution to equation (33) is $-2p^2\bar{v}$. Again, to dominant order in c_b for configuration B, the variables $\{m_i\}$ are $m_0 \rightarrow 6G_{00}^0$, $m_1 \rightarrow 6G_{01}^0$, $m_2 \rightarrow -G_{00}^0$, $m_3 \rightarrow 6G_{00}^0$, and the corresponding contribution to equation (33) reads $(1 - p^2)/(6G_{00}^0)$. Recalling the definition $p = 1 - c_b$, we infer that in the low-concentration limit

$$\bar{v} = c_b/(6G_{00}^0). \quad (35)$$

For $\bar{v} = 0$ and $\bar{\sigma} = 1$, the GF G_{00}^0 in equation (35) is expressed via the Watson integral $I_W \simeq 1.51$, namely $6G_{00}^0 = I_W$ [11]. The total rate of adsorption of A particles in the kinetics equation (10) is equal to $\bar{v}_{\text{eff}} = 6\bar{v}$, so

$$\bar{v}_{\text{eff}} = 6c_b/I_W.$$

This is nothing but the result by Montroll and Weiss for the rate of absorption with one centre of diffused particles on a regular lattice [16], presenting the lattice version of the Smoluchowski theory [17], and the one-site coherent potential approximation (CPA) result [11] as well. Equation (35), considered as an equation for \bar{v} for all c_b and prescribed $\bar{\sigma} = 1$, yields a monotonically increasing solution versus concentration

c_b , so that $\bar{v}(c_b) > 1$ at $c_b > 0.5$. Actually, for $\Gamma = 1$, the value \bar{v} should not exceed unity, as this is the diffusion-controlled rate for transitions along one bond. By contrast, the cluster approach with two possible configurations A and B on the one hand yields the CPA in the low-density limit, and on the other hand does not suffer from the aforementioned shortcoming as the density increases. Acceptable roots of equation (33) lie within the range $0 \leq \bar{v} \leq \Gamma$ for $0 \leq c_b \leq 1$; moreover, at $\Gamma \rightarrow \infty$, the rate \bar{v} renormalizes, becoming much smaller than Γ . To see this, we should bear in mind that $\bar{\sigma} = 1$ solves the self-consistent equation (30), so equation (33) is the only equation in hand. For configuration A, $\Delta_0 = 0$ and the variables $\{m_i\}$ take on values $m_0 = 1 - 6\bar{v}G_{00}^0$, $m_1 = 6\bar{v}G_{01}^0$, $m_2 = \bar{v}G_{01}^0$, $m_3 = 1 - 6(1 + \bar{v})G_{01}^0$. Leading terms coming from configuration B are proportional to Γ , i.e. $m_0 = 6\Gamma G_{00}^0$, $m_1 = 6\Gamma G_{01}^0$, $m_2 = -\Gamma G_{01}^0$, $m_3 = \Gamma g^0$, giving the following contribution to equation (33): $(1 - p^2)/(6G_{01}^0)$. Thus, the self-consistent equation for \bar{v} reduces to

$$\frac{1 - p^2}{6G_{01}^0} + p^2 \bar{v} \frac{(1 + \bar{v})(m_0 + 6m_2) - m_1 + m_3}{M} = 0. \tag{36}$$

It is possible to find an analytical solution to equation (36) in the limit $c_b \rightarrow 0$. Then, just as we had for the case with finite Γ , we expect that $\bar{v} \rightarrow 0$, so the expressions for $\{m_i\}$ are simplified to $m_0 \rightarrow 1$, $m_1 \rightarrow 0$, $m_2 \rightarrow 0$, $m_3 \rightarrow 1$, and

$$\bar{v} = c_b / (6G_{01}^0). \tag{37}$$

By equation (10), the GF for the effective lattice, G_{01}^0 , with $\bar{\sigma} = 1$, $\bar{v} \rightarrow 0$ is connected with I_W , leaving the final result

$$\bar{v} = c_b / (I_W - 1). \tag{38}$$

5. Discussion of numerical results

For arbitrary parameter Γ and concentrations c_b , we seek a solution to equations (30) and (33) numerically. The needed Green functions are provided in the appendix. Referring to figure 2, we see that, at fixed concentration c_b , the effective diffusion rate $\bar{\sigma}(\Gamma)$ increases with Γ . The cause of this behaviour is the percolation cluster totally reflecting the particles of A when $\Gamma = 0$. This means that in the proximity of the cluster, the flow of A particles equals zero. When Γ is increased, the reflecting property of the cluster is replaced with an adsorbing one, providing a flow at the border of the cluster. A part of this flow will be adsorbed, giving augmentation of the aggregate, and the other part leaks through the solid B structure causing penetration. The case $\Gamma \rightarrow \infty$ yields $\bar{\sigma} = 1$ overall, except at $c_b = 1$. A large diffusion rate is due to surviving particles of A that do not 'know' their fate and have unit diffusion rate.

The first thing that happens when looking at figure 3 is a quick rise in \bar{v} at small values of c_b . Given a value of the parameter Γ , the rate curve $\bar{v}(c_b)$ at a very low concentration c_b starts out from zero with slope

$$\frac{\Gamma}{I_W + (\Gamma - 1)(I_W - 1)} \tag{39}$$

and behaves as in gas-phase reactions. As the concentration increases, the enhancement of $\bar{v}(c_b)$ for larger Γ is observed. The effect increases with the value of Γ , and at $\Gamma \simeq 2$, the function $\bar{v}(c_b)$ undergoes considerable derivative $d\bar{v}/dc_b$, at a critical concentration $c_b^*(\Gamma)$; see figure 4. In the language of phase transition theory, this could be called a first-order transition. A sharp increase in \bar{v} shows that some structural transition in the solid phase occurs, to become linked and ramified in order to provide, for a small value of c_b^* , a large rate of adsorption in comparison with the rate of effective diffusion. There is no reason to suppose that this effect disappears if more accurate statistics $f(\theta)$ are involved or different lattices are considered.

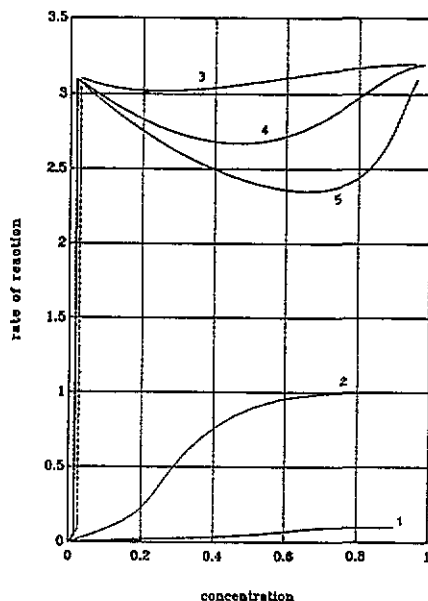


Figure 3. The effective rate of deposition of A particles, \bar{v} , as a function of concentration of solid phase of B for the set of values of the parameter Γ as in figure 2, except for $\Gamma = 0$: (1) 0.1, (2) 1, (3) 10, (4) 100, (5) 1000.

It seems plausible to assume that the observed behaviour in $\bar{v}(c_b)$ is connected with spanning clusters since the sharp increase in $\bar{v}(c_b)$ resembles the observed behaviour in the $P_\infty(c)$ near the percolation threshold [18]. The effective-medium approximation provides no means to gain information about inherent fluctuations in the geometrical shape of the aggregate, except for averaged or smoothed structure, with the concentration c_b^* being the only quantitative measure of the structure.

As we go to $\Gamma \rightarrow \infty$, the rate $\bar{v}(c_b)$ renormalizes, becoming independent of Γ . The corresponding curves for different Γ and small c_b are slightly displaced towards zero from each other without any substantial effect on the shape.

6. Conclusion and summary

The condition $\bar{\sigma} = 0$ in the models with pure diffusion [6, 8] is known to indicate the existence of the percolation structure. The effect observed in this paper can be

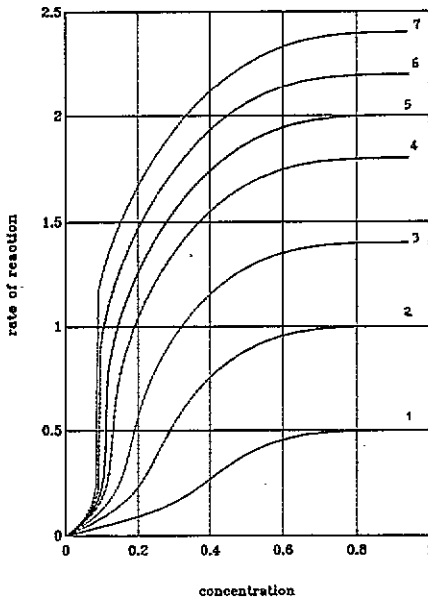


Figure 4. The effective rate of deposition of A particles, \bar{v} , as a function of concentration of solid phase of B for different values of the parameter Γ : (1) 0.5, (2) 1, (3) 1.4, (4) 1.8, (5) 2, (6) 2.2, (7) 2.4. The rate, \bar{v} , jumps almost discontinuously for $\Gamma \approx 2$.

thought of as a chemical analogue for the geometrical phase transition occurring in an ensemble with chemically active particles. A sharp increase in the effective rate of adsorption is likely to be a manifestation of the formation of structures somewhat similar to the fractal DLA structures observed in computer simulations [2, 3].

To describe this effect, a model has been formulated, viz. equation (9) with $\Gamma > 1$. The effective rate $\bar{v}(c_b)$ is shown to exhibit a critical behaviour when

$$\Gamma > \Gamma^* \approx 2. \quad (40)$$

For small Γ , the dependence $\bar{v}(c_b)$ is rather smooth, but when Γ approaches Γ^* , the dependence of \bar{v} on c_b becomes more and more sharp, so that for Γ above Γ^* , $\bar{v}(c_b)$ jumps almost discontinuously at the critical concentration $c_b^*(\Gamma)$. This state is critical in the sense of first-order phase transitions. The $c_b^*(\Gamma)$ shifts towards zero with increasing Γ , becoming $c_b^*(\infty) \approx 0.016$. That is, all incoming flow of particles is adsorbed when the solid phase occupies about 1.5% of the whole volume. As in the case of the percolation problem, the other properties of the internal structure of the adsorbate, except the critical concentration, are not known within the EMT.

It is by no means certain that the EMT can be taken for granted, despite the fact that the observed structures occur at the low-concentration limit where the EMT is likely to be valid [6]. The main question addressed here is, why does the proposed theory show a sharp increase in the function $\bar{v}(c_b)$ at such small values of c_b ? A more subtle theory than the small-cluster self-consistent one is required to describe the occurrence of ramified structures. Our point of view can only be justified by the utility of the effective-medium approaches in the theory of first-order phase transitions, both for equilibrium and for percolating systems, where the large-cluster problem is also ignored due to its unacceptable labour.

The second fortunate feature of this paper is in exploring transport coefficients \bar{v} and $\bar{\sigma}$ for the model with $\Gamma \leq 1$. The effective-medium formalism provides an alternative tool for calculating the concentration dependence of the effective rates of local reaction, when $\Gamma \leq 1$, along with the formalism in [19]. The self-consistent equations relative to effective diffusion coefficient, $\bar{\sigma}$, and effective chemical rate, \bar{v} , present a transcendental algebraic equation, which has been solved analytically in the case $c_b \rightarrow 0$. A lattice version of the Smoluchowski result is reproduced at $\Gamma = 1$ and $c_b \rightarrow 0$ as well as judicious behaviour of \bar{v} that becomes less than unity. In this respect, the cluster approach improves the concentration dependence of the one-site CPA model [11]. Though the calculations have been done for the zero-frequency limit, $\omega = 0$, to get a temporal dependence of \bar{v} is also possible.

Thus far, the model has been restricted to the situation with fixed concentration of the B particles, the so-called quasi-stationary approximation. It is important also to enquire about the deposition process when the rates inherit their temporary dependence on time from the concentration c_b . So, we should turn to equation (5a) and write, on averaging, the rate of change $c_{b,j} = \langle n_{b,j} \rangle$ as

$$\partial_t c_{b,j} = d_a c_{a,j} \sum_e \bar{v}_{j+e} = d_a c_{a,j} (\Delta \bar{v}_j + 6\bar{v}_j) \quad (41)$$

where $c_{a,j} = \langle n_{a,j} \rangle$, Δ is the three-dimensional Laplacian and the second form of the equation helps to reveal its basic properties such as the diffusional spreading of B particles and their growth. In addition, equation (41) has been generalized to non-uniform making use of the arguments of section 4.1, i.e. $\bar{v}_j = \bar{v}(c_{b,j})$. Within this context, the concentration of A particles is seen to play a role analogous to that of the diffusion coefficient. In what follows, a non-uniform profile in $c_{a,j}$ induces instability in the growth of the solid phase, i.e. places of the B phase with a small $c_{a,j}$, being far from the source of A particles, have a small rate of motion, and places near to the source move more rapidly. As a result, the structure can grow into a set of fingers which are pores themselves. Incidentally, the instability can be suppressed by making the profile $c_{a,j}$ more or less uniform. This happens in models with ballistic motion of A particles, when the convective flow is proportional to the concentration $c_{a,j}$ (not gradient of the concentration) and $c_{a,j}$ is practically spatially uniform. This fact is in qualitative agreement with the simulation of ballistic deposition [20], where the thickness ξ is found to scale with aggregate average size as $\xi \simeq l^{1/3}$ (for the three-dimensional case) in comparison with larger thickness $\xi \simeq l$ in the diffusion-limited mode [20].

In conclusion, we note that the dependence $\bar{\sigma}(\Gamma)$ can be observed in electrochemical experiments that are known to be sensitive to the morphology of the deposits [21].

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Appendix

Here, the Green functions on a simple cubic lattice will be presented in a form that provides a minimum cost in numerical calculations. Let us write the expression for

the GF as the Fourier integral ($\omega = 0$)

$$G_{00}^0 = \frac{J_0}{\bar{\sigma}} \quad (A1)$$

$$J_0 = \frac{1}{\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi \frac{d\phi_1 d\phi_2 d\phi_3}{6\psi + 6 - 2 \sum_{d=1}^3 \cos \phi_d}.$$

Here, a dimensionless variable $\psi = \bar{v}/\bar{\sigma}$ is introduced. The integral over two variables, for instance $d\phi_2$ and $d\phi_3$, can be done by hand [22], so that

$$J_0(\psi) = \frac{2}{\pi^2} \int_0^\pi \frac{d\phi_1}{6\psi + 6 - 2 \cos \phi_1} K \left(\frac{4}{6\psi + 6 - 2 \cos \phi_1} \right) \quad (A2)$$

where $K(z)$ is the total elliptic integral of the first kind [23]. Note that $J_0(0) = I_W/6$, where $I_W \simeq 1.51$ is the Watson integral, and $J_0(\psi) \rightarrow 1/\psi$ at $\psi \rightarrow \infty$, because $K(0) = \pi/2$. The GF G_{01}^0 can be conveniently expressed as $G_{01}^0 = J_1/\bar{\sigma}$, where $J_1(\psi)$ is related to $J_0(\psi)$ by equation (10), i.e. $J_1 = J_0 - (1 - \psi J_0)/6$. Analogously, an expression for $G_{00}^0 - G_{16}^0$ can be reduced to a one-dimensional integral

$$G_{00}^0 - G_{16}^0 = J_2/\bar{\sigma}$$

as

$$J_2(\psi) = \frac{2}{\pi^2} \int_0^\pi \frac{d\phi_1(1 - \cos 2\phi_1)}{6\psi + 6 - 2 \cos \phi_1} K \left(\frac{4}{6\psi + 6 - 2 \cos \phi_1} \right). \quad (A3)$$

In terms of variables ψ and $\bar{\sigma}$, equation (30) represents a quadratic equation relative to $\bar{\sigma}$. On substituting its solution $\bar{\sigma} = \bar{\sigma}(\psi)$ into equation (33), we obtain an algebraic transcendental equation relative to variable ψ . The function $M(\psi, \bar{\sigma}(\psi))$ in equation (33) has zeros in the range $0 \leq \psi \leq \Gamma$, so one should find a common denominator, to seek a solution to equation (33) as a root of the numerator of the resultant fraction.

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