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Competitive diffusion sinks and precipitation on dislocations*

Marshall Fixman
Department of Chemistry, Yale University, New Haven, Connecticut 06520
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The kinetics of stress-assisted precipitation on dislocations is investigated on the basis of a two-dimensional lattice analog of Ham's parallel-cylinder model. The rate of precipitation was calculated for site fractions of sinks up to 0.25 by exact methods (for small systems containing up to 36 sinks) and by several approximate methods. For a random array of sinks the rate of precipitation was found to be much slower than the first-order kinetics appropriate to a periodic array, contrary to a common belief.

I. INTRODUCTION

It is widely believed[1-6] that simple models of the precipitation of point defects at randomly distributed dislocation lines must yield first-order kinetics in the later stages. We have reinvestigated this problem on the basis of a lattice model of competitive diffusion to sinks and find a contrary result, namely, that the kinetics is slower than first order for a random distribution of sinks.

The source of the conventional belief in first-order kinetics seems to be the analysis of Ham,[1] who showed that a regular array of parallel dislocation lines gave first-order precipitation kinetics after a quite short induction period, and who then went on to argue that a random array of dislocation lines would not yield significantly different kinetics. On this basis, he concluded that Harper's rather intuitive generalization[7] of Cottrell and Bilby's short-time equations[8] for stress-assisted precipitation was faulty.

Harper had suggested that the fraction $W(t)$ of impurities remaining in solution would follow the equation $W(t)=\exp(-at^b)$, with a and b inferred from the short-time equations of Cottrell and Bilby. Thus $b=\frac{2}{3}$ if the attraction energy between an impurity atom and a dislocation line varies with distance r as r^{-1}. Because on the one hand, Harper's equation often fits experimental data quite well,[4] and on the other hand is properly regarded as without theoretical foundation, it has been assumed that the basic model of stress-assisted precipitation is at fault, and more elaborate models of the short-ranged interaction between impurity and dislocation have been proposed.[4] Whatever the merit of these proposals, we wish to argue here that they have not been adequately motivated, and that, in fact, a random array of dislocation lines will give precipitation kinetics that are much slower than first order.

Our model is a lattice equivalent of that examined by Ham[1] who replaced each dislocation line and its associated stress field by a cylinder of radius R, on the surface of which the concentration of impurities is required to vanish for $t>0$. Ham showed that the precipitation rate on an isolated dislocation line, that attracts an impurity with energy $E=-kT\sigma/r$, is quite close to the precipitation rate on the cylinder after a short induction period, if R is chosen approximately equal to σ. The induction time is of order R^2/D, where D is the diffusion constant. For short times the fluxes are proportional to $t^{-1/3}$ for the dislocation, and $t^{-1/2}$ for the cylinder. For our lattice model the initial flux is finite.

The failure of lattice kinetics to agree with continuum kinetics at short times is not a serious problem for the low concentration of sinks, characteristic of the physical problem. Numerical results confirm one's expectation that the time period over which the bulk of impurity is exhausted moves to larger values as the concentration of sinks decreases, and discrepancies in the initial precipitation rate move off the time scale of interest.

We have used a finite lattice with periodic boundary conditions because of several advantages that this model offers in comparison with a finite or infinite continuum model with cylindrical sinks.[9] The advantage of a lattice model versus a continuum is first that the boundary condition of vanishing concentration on the surface of a cylinder is (practically) impossible to satisfy exactly for a finite sink concentration. It is true that the boundary condition can be satisfied easily to a very high accuracy when the sinks are far apart, as they will be for low sink densities, but we wanted to have exact results available to test approximation methods. Second, the use of periodic boundary conditions ensures that the kinetics will become first order at sufficiently long times, and therefore the model is biased against, rather than for, the point to be demonstrated. As the lattice size increases, the first-order limiting behavior moves to longer times, off the scale of physical interest [here considered to be (5–95)% precipitation of impurities].

In summary, a finite lattice model with periodic boundary conditions affords the possibility of exact calculation, and misbehavior at short times is removed from the time scale of interest for low sink concentrations, and at long times for a sufficiently large sample. The calculations would have been easier for a continuum model, if plausible approximations were allowed, mainly because good polynomial approximations for the continuum Green's functions (cylindrical Bessel functions) are available. For the finite lattice, the Green's functions require fairly tedious summation over the first Brillouin zone.

In Sec. II, the diffusion equations are set up and Laplace transformed. The determination of fluxes into I sinks on a finite periodic lattice is reduced to a set of I linear equations, and these equations are solved and the inverse transform computed by numerical means. An average over a random distribution of sinks then provides exact results with which approximations may be compared. These approximations are (i) use of a regular array of sink locations, (ii) evaluation of the flux into a sink as the flux into an isolated sink, reduced by the mean concentration of impurities, or (iii) the average t-matrix approximation, in which all fluxes are replaced by the ensemble average flux. The approximate methods are surveyed in Sec. III, and numerical results and discussion are presented in Sec. IV.

II. DIFFUSION EQUATIONS AND THEIR FORMAL SOLUTION

The system of interest is a square lattice of M^2 sites labeled by their vector positions $\vec{r}$. The sites at $\vec{r}=\vec{R}_i$, $i=1,2,\ldots,I$ are sinks at which diffusing impurity atoms are absorbed. At the sinks, the concentration $P(\vec{r},\tau)$ of impurity atoms (the number of atoms per site) is zero for all times $\tau \geqslant 0$. Elsewhere, the concentration $P(\vec{r},\tau)$ is initially unity, and subsequently decreases due to the diffusion of impurity atoms toward the sinks.

Periodic boundary conditions are imposed along the orthogonal x and y directions; sites x and $x+Ma$, where a is the site spacing, are physically identical.

In this section we first set up the basic diffusion equations in reduced variables, then consider their Laplace transformation and the scheme for numerical inversion, and finally express the formal solution for the sink strengths in terms of the Green's function that connects any pair of sinks.

A. Basic equations and reduced variables

At any lattice site not occupied by a sink, the impurity concentration is taken to obey the two-dimensional diffusion equation

$$\frac{\partial P(\vec{r},\tau)}{\partial \tau} = D\nabla^2 P(\vec{r},\tau), \quad \tau > 0\,. \tag{2.1}$$

The operator ∇^2 has to be interpreted as a finite difference operator,

$$\nabla^2 \equiv (4/a^2)\delta^{(2)}, \quad \delta^{(2)} \equiv \delta_x^{(2)} + \delta_y^{(2)}, \tag{2.2}$$

and with an obviously abbreviated notation for the arguments of P,

$$\delta_x^{(2)}P(x) \equiv \tfrac{1}{4}[P(x+a)+P(x-a)-2P(x)]\,. \tag{2.3}$$

The factor $\frac{1}{4}$ is introduced to simplify the appearance of the eigenvalues of $\delta^{(2)}$. The quantity $(4D/a^2)$ that appears in the diffusion equation, after (2.2) is introduced into (2.1), has the units of reciprocal time, and it proves convenient to use a reduced time variable t,

$$t \equiv (4D/a^2)\tau \tag{2.4}$$

and

$$\frac{\partial P(\vec{r},t)}{\partial t} = \delta^{(2)}P(\vec{r},t) \tag{2.5}$$

still in the absence of a sink at $\vec{r}$.

With the explicit introduction of sinks, we have the following equation applicable at all sites:

$$\frac{\partial P(\vec{r},t)}{\partial t} = \delta^{(2)}P(\vec{r},t) - \sum_{i=1}^{I} F_i(t)\delta(\vec{r}-\vec{R}_i), \tag{2.6}$$

where $F_i(t)$ is the sink strength or flux into i, that is, $F_i(t)$ is the number of impurity atoms per unit of t absorbed by the ith sink.

The total number of impurity atoms absorbed by the sinks is

$$N(t) = \sum_{\vec{r}} [P(\vec{r},0) - P(\vec{r},t)], \quad N(\infty) = M^2 - I \tag{2.7}$$

and

$$\frac{dN(t)}{dt} = \sum_{i=1}^{I} F_i(t)\,. \tag{2.8}$$

Our objective is the calculation of an ensemble average of any $F_i(t)$ over appropriate distributions of the sink locations. Primary attention is given to a random distribution. The evolution of $N(t)$ can then be obtained from Eq. (2.8).

B. Laplace transformation and inversion

Let the Laplace-transformed concentrations and fluxes be

$$p(\vec{r},s) \equiv \int_0^\infty e^{-st}P(\vec{r},t)\,dt, \tag{2.9}$$

$$f_i(s) \equiv \int_0^\infty e^{-st}F_i(t)\,dt\,. \tag{2.10}$$

The transform of $N(t)$ is obtained from Eq. (2.8):

$$\begin{aligned} n(s) &\equiv \int_0^\infty e^{-st} N(t)\,dt \\ &= \int_0^\infty e^{-st}\left(\int_0^t \frac{dN(t')}{dt'}dt'\right) dt \\ &= s^{-1}\sum_{i=1}^{I} f_i(s). \end{aligned} \tag{2.11}$$

The transforms $f_i(s)$ were evaluated at a discrete set of positive values of s, by exact and approximate methods still to be described, and then the required inverse transforms were obtained with the inversion algorithm of Bellman *et al.*[10] Application of this algorithm to a transform such as Eq. (2.10) rests on the assumption that $F_i(t)$ can be approximated by a finite sum of exponentials with equally spaced decay rates. Then a change of variables to $x \equiv e^{-t}$ implies that $F_i(t)$ can be approximated by a polynomial in x, and Gauss-Legendre integration is used to determine the integral over x. The result of this approach is a linear relation between $F_i(t)$ and $f_i(s)$ for a finite set of discrete arguments:

$$\beta F_i(-\beta \ln x_k) = \sum_{l=1}^{J} A_{kl} f_i\left(\frac{l}{\beta}\right), \tag{2.12}$$

where β is an arbitrary positive number, and the x_k and A_{kl} are determined from the roots and weights of Gauss-Legendre integration by methods (and FORTRAN programs), presented by Bellman *et al.*[10] The constant β can be varied to permit calculation of $F_i(t)$ on a proper time scale, and the results of the calculation can be checked by varying size J of the basis set. If J is too small, oscillations appear in $F_i(t)$ at long times. The value $J = 12$ was used for all calculations; some residual oscillations may be marginally visible on the graphs of exact results at low sink densities and long times.

Laplace transformation of Eq. (2.6) gives

$$s p(\vec{r}, s) - P(\vec{r}, 0) = \delta^{(2)} p(\vec{r}, s) - \sum_{i=1}^{I} f_i(s)\delta(\vec{r} - \vec{R}_i). \tag{2.13}$$

The solution for $p(\vec{r}, s)$ may be obtained explicitly in terms of the Green's function $g(\vec{r}, \vec{r}\,')$ that satisfies

$$(s - \delta^{(2)}) g(\vec{r}, \vec{r}\,') = \delta(\vec{r} - \vec{r}\,'), \tag{2.14}$$

namely,

$$p(\vec{r}, s) = \sum_{\vec{r}\,'} g(\vec{r}, \vec{r}\,')\left(P(\vec{r}\,', 0) - \sum_{i=1}^{I} f_i(s)\delta(\vec{r}\,' - \vec{R}_i)\right) \tag{2.15}$$

or

$$p(\vec{r}, s) = s^{-1} - \sum_{\vec{r}\,'} g(\vec{r}, \vec{r}\,') \sum_{i=1}^{I} h_i(s)\delta(\vec{r}\,' - \vec{R}_i), \tag{2.16}$$

where

$$h_i(s) = 1 + f_i(s). \tag{2.17}$$

Equation (2.16) follows from the fact that $P(\vec{r}, 0)$ is unity except at the sinks, where it vanishes, and from the consequence of Eq. (2.14), that $g(\vec{r}, \vec{r}\,')$ summed over $\vec{r}\,'$ is s^{-1}. Evaluation of Eq. (2.16) for $\vec{r}$ equal to one of the sink positions R_j gives

$$\sum_{i=1}^{I} g(\vec{R}_j, \vec{R}_i) h_i(s) = s^{-1}, \tag{2.18}$$

a set of linear equations for the $h_i(s)$ readily solvable by numerical means. Evaluation of the Green's function is summarized below.

C. Green's function

The periodic boundary conditions imposed on the lattice imply that $g(\vec{r}, \vec{r}\,')$ is given by

$$g(\vec{r}, \vec{r}\,') = \sum_{\vec{k}} g_{\vec{k}} \exp[i\vec{k} \cdot (\vec{r} - \vec{r}\,')], \tag{2.19}$$

where k_x and k_y run over the same set of values (in units such that $a \equiv 1$),

$$k_x = 2\pi l_x / M, \quad l_x = 0, 1, \ldots, M-1, \tag{2.20}$$

with

$$\delta(\vec{r} - \vec{r}\,') = M^{-2} \sum_{\vec{k}} \exp[i\vec{k} \cdot (\vec{r} - \vec{r}\,')]$$

and

$$\delta_x^{(2)} \exp(ik_x x) = -(\sin^2 \tfrac{1}{2}k_x) \exp(ik_x x).$$

Equation (2.14) and (2.19) give

$$g_{\vec{k}} = M^{-2}(s + \sin^2 \tfrac{1}{2}k_x + \sin^2 \tfrac{1}{2}k_y)^{-1}. \tag{2.21}$$

The Green's function was calculated from Eqs. (2.19) and (2.21); the first Brillouin zone, of course, has considerable symmetry that reduces the number of terms to be summed.

We will return to the exact calculations, which were carried through for both regular and random distributions of sinks, in Sec. IV. In Sec. III two approximate methods will be discussed.

III. APPROXIMATE METHODS

The two approximations both belong in the general class of mean-field theories. The first and best approximation was used by Harper[7] and amounts, in its baldest form, to the assertion that the mean flux into a sink is reduced by competition in the same ratio that the mean impurity concentration is reduced. This concentration $C(t)$ is defined in terms of $N(t)$, the number of absorbed impurities, by

$$C(t) = [N(\infty) - N(t)]/M^2 \tag{3.1}$$

and, therefore,

$$\frac{dC(t)}{dt} = -\rho F(t), \tag{3.2}$$

where $F(t)$ is the flux into a single sink, averaged over the sink distribution with mean density $\rho = I/M^2$. With $k(t)$ defined as the flux into an isolated sink in an infinite system [for which $C(t)$ is therefore fixed at $C(0) \equiv 1$], the assumption is that

$$F(t) = k(t)C(t). \tag{3.3}$$

Here, $C(t)$ is less than unity for all times; $C(0) = 1 - \rho$. Equation (3.2) gives

$$\frac{d\ln C(t)}{dt} = -\rho k(t). \tag{3.4}$$

Equation (3.4) was criticized by Ham[1] on two grounds, one of which [namely, the form used for $k(t)$], is irrelevant to the present discussion. The relevant objection was simply that Eq. (3.4) is inadequate for a random distribution of sinks, but evidence against the approximation actually consisted of a comparison with results for an approximate model of a regular sink distribution. We will see that Eq. (3.4) is a much better approximation for a random system than is the regular array.

The second approximation consists in the neglect of fluctuations in the sink strengths. Equation (2.18) then gives

$$\bar{h}_i(s) = 1 + f(s) = s^{-1}\left(\left\langle\left\langle \sum_{i=1}^{I} g(\vec{R}_j, \vec{R}_i)\right\rangle\right\rangle\right)^{-1}, \tag{3.5}$$

where the average is taken over all sink distributions such that $\vec{R}_i \neq \vec{R}_j$, unless $i = j$. Equation (3.5) then gives [since the sum of $g(\vec{r}, \vec{r}\,')$ over all $\vec{r}\,'$ is s^{-1}]

$$1 + f(s) = \rho' + s(1 - \rho')g(0), \tag{3.6}$$

where

$$\rho' \equiv (I - 1)/M^2, \quad g(0) \equiv g(\vec{r}, \vec{r}).$$

Equations (3.2) and (3.6), with $F(t)$ the inverse transform of $f(s)$, provide $C(t)$. This approximation will be shown equivalent to the "average t-matrix approximation" of imperfect crystal theory,[11] for which considerable discussion already exists. It will be seen that the approximation is not very good for long times.

A. Isolated sink approximations

Here, some additional discussion of the isolated sink approximation, Eq. (3.3), will be given in order to see how the approximation could be generalized and improved on the basis of a hierarchy of conditional averages of Eq. (2.6). The development of such hierarchies has been a standard approach in statistical mechanics since the work of Kirkwood and Yvon on fluids, forty years ago.[12] The utility of the approach depends, of course, on how well the hierarchy can be truncated.

A complete average of the basic diffusion equation [Eq. (2.6)], over all sink positions gives Eq. (3.2). The isolated flux approximation, Eq. (3.3), may be regarded as a closure of the hierarchy at the zeroth level.

A partial or conditional average of Eq. (2.6) over all sink positions except the first, which is fixed at $\vec{R}$, gives

$$\frac{\partial P(\vec{r}, t; \vec{R})}{\partial t} = \delta^{(2)}P(\vec{r}, t; \vec{R}) - F(t)\delta(\vec{r} - \vec{R}) - \rho(\vec{r}; \vec{R})F(\vec{r}, t; \vec{R}). \tag{3.7}$$

Here, the argument $\vec{R}$ following the semicolon indicates a conditional average given a sink fixed at $\vec{R}$. Thus, $\rho(\vec{r}; \vec{R})$ is the conditional mean density of sinks at $\vec{r}$, and $F(\vec{r}, t; \vec{R})$ is the conditional mean flux into a sink at $\vec{r}$.

We now wish to consider large systems for which it is meaningful to speak of the limit of $F(\vec{r}, t; \vec{R})$ as $|\vec{r} - \vec{R}| \to \infty$. This limit must be the unconditional mean flux $F(t)$. For small $|\vec{r} - \vec{R}|$, competition from the flux at the origin must reduce $F(\vec{r}, t; \vec{R})$ below its asymptotic value. Likewise $P(\vec{r}, t; \vec{R})$ has an asymptotic limit, namely the unconditional average $C(t)$, and will be reduced below this limit for small $|\vec{r} - \vec{R}|$. If it is assumed that $P(\vec{r}, t; \vec{R})$ and $F(\vec{r}, t; \vec{R})$ are decreased in proportion, i.e., that

$$F(\vec{r}, t; \vec{R})/F(t) \cong P(\vec{r}, t; \vec{R})/C(t), \tag{3.8}$$

then the hierarchy has been closed at its first level (one sink position has been reserved from averaging). The hierarchy is closed because Eq. (3.7) contains, when (3.8) is used, just a single unknown function, $P(\vec{r}, t; \vec{R})$, and sufficient boundary conditions to determine it. The method of solution will now be investigated in more detail, and Eq. (3.8) will be shown to imply the isolated flux approximation *if* $\rho(\vec{r}; \vec{R})$ is a random distribution of sinks in the neighborhood of $\vec{R}$.

Let $q(\vec{r}, t)$ be defined by

$$P(\vec{r}, t; \vec{R}) = C(t)q(\vec{r}, t). \tag{3.9}$$

The boundary conditions are

$$q(\vec{r}, t) = \begin{cases} 0 & \text{if } \vec{r} = \vec{R}, \quad t \geq 0, \\ 1 & \text{if } \vec{r} \neq \vec{R}, \quad t = 0, \\ 1 & \text{if } |\vec{r} - \vec{R}| \to \infty, \quad t > 0. \end{cases} \tag{3.10}$$

Further, let $K(t)$ and $k(t)$ be defined by

$$C(t)=C(0)\exp\left(-\int_0^t K(t)\,dt\right),\qquad K(t)=\rho k(t)\,. \tag{3.11}$$

It is *not yet* implied that $k(t)$ is given by the isolated sink approximation, although this will be shown under certain conditions. However, we do know from Eqs. (3.2) and (3.11) that

$$\frac{d\ln C(t)}{dt}=-\rho k(t)=\frac{-\rho F(t)}{C(t)},\qquad F(t)=k(t)C(t)\,. \tag{3.12}$$

That is, Eq. (3.3) holds as a matter of formal definition. Substitution from Eqs. (3.8), (3.9), and (3.11), (3.12) into Eq. (3.7) gives

$$\frac{\partial q(\vec{r},t)}{\partial t}=\delta^{(2)}q(\vec{r},t)-k(t)\delta(\vec{r}-\vec{R})+k(t)[\rho-\rho(\vec{r};\vec{R})]q(\vec{r},t)\,. \tag{3.13}$$

It is now obvious that *if* $\rho(\vec{r};\vec{R})=\rho$ for all $\vec{r}\neq\vec{R}$, then Eq. (3.13), together with the boundary conditions (3.10), imply that $k(t)$ is the flux into an isolated sink with concentration at infinity fixed at unity. If there is a positive clustering of sinks, Eq. (3.13) implies a lower value of $k(t)$.

If the hierarchy is not closed at the first level with the approximation, Eq. (3.8), then another source will appear on the right-hand side of Eq. (3.13); this new source will have a value that varies with $\vec{r}$ as the difference between the left- and right-hand sides of Eq. (3.8). If then, an approximation like Eq. (3.8) is applied at the second level of the hierarchy where two sink positions are reserved from averaging, one finds that the two sink strengths are the same as for an isolated pair, but reduced by a factor $C(t)$. Presumably, this will be a better approximation than Eq. (3.8) for small $|\vec{r}-\vec{R}|$, but the additional numerical work required to verify an improvement has not been done.

B. Equal flux approximation

Here, the equal flux approximation will be shown equivalent to the average t-matrix approximation.[11] Because this approximation is relatively poor at long times, and because this approximation and closely related ones have been extensively reviewed in the literature,[11] we will not discuss its merits, apart from a comparison with exact results in Sec. IV.

To apply the average t-matrix approximation, we start with Eq. (2.13) for the concentration $p(\vec{r},s)$. Let the fluxes $f_i(s)$ be replaced by $\lambda p(\vec{R}_i,s)$, where λ will be made to approach infinity. In this revised model, the impurity atoms are initially distributed uniformly over all sites, including sink locations. But in the limit $\lambda\to\infty$, the impurity atoms at sink locations disappear with rate $\lambda e^{-\lambda t}$, and we expect to find agreement with the original version of the model if $\lambda p(\vec{R}_i,s)$ is compared with $1+f_i(s)$, or $\lambda P(R_i,t)$ with $\delta(t)+F_i(t)$.

For the revised model, Eq. (2.13) becomes

$$(s-\delta^{(2)}+V)p(\vec{r},s)=P(\vec{r},0)=1\,, \tag{3.14}$$

$$V\equiv\lambda\rho(\vec{r}),\quad \rho(\vec{r})=\sum_{i=1}^{I}\delta(\vec{r}-\vec{R}_i)\,. \tag{3.15}$$

In the t-matrix approximation, the average Green's function $\langle(s-\delta^{(2)}+V)^{-1}\rangle$ is evaluated in the limit $\lambda\to\infty$ as

$$\langle(s-\delta^{(2)}+V)^{-1}\rangle=(s-\delta^{(2)}-\Sigma_0)^{-1}\,, \tag{3.16}$$

with a self-energy Σ_0 given by

$$\Sigma_0=-\rho[(1-\rho)g(0)]^{-1},\quad g(0)\equiv g(\vec{r},\vec{r})\,. \tag{3.17}$$

It follows from Eq. (3.14) that

$$p(s)\equiv\langle p(\vec{r},s)\rangle=(s-\Sigma_0)^{-1}\,, \tag{3.18}$$

while a direct average of Eq. (2.13) gives [with $\langle f_i\rangle$ replaced by $1+\langle f_i\rangle=1+f(s)$ for the reason already given]

$$sp(s)+\rho[1+f(s)]=1\,. \tag{3.19}$$

Therefore,

$$1+f(s)=(\rho-\rho s/\Sigma_0)^{-1}=[\rho+s(1-\rho)g(0)]^{-1} \tag{3.20}$$

after substitution from Eq. (3.17). This agrees with the result already given in Eq. (3.6) for large systems, where $\rho'\to\rho$.

IV. RESULTS

A. Numerical results

Results for $K(t)=-d\ln C(t)/dt$ are presented in Figs. 1–3 for the sink densities $\rho=2^{-2}$, 4^{-2}, 6^{-2}.

The exact results shown were computed from Eqs. (2.12) and (2.18) for systems with 36 sinks. Calculations for the same sink density on systems of 16 and 25 sinks showed a slight decrease in $K(t)$ values at large t (i.e., at 95% precipitation) between these two systems, but no further decrease on increase of the number of sinks to 36. However, at the lower sink density $\rho=8^{-2}$ variation of $K(t)$ between $I=16$ and $I=25$ was more substantial ($\log_{10}K_{25}/K_{16}\simeq-0.05$ at 95% precipitation), and because the larger value of M required for given I at lower densities made the calculations rather lengthy, we have contented ourselves with the three densities shown.

Values of $C(t)$ and $dC(t)/dt$ used to calculate the exact $K(t)$ are averages over four random arrays

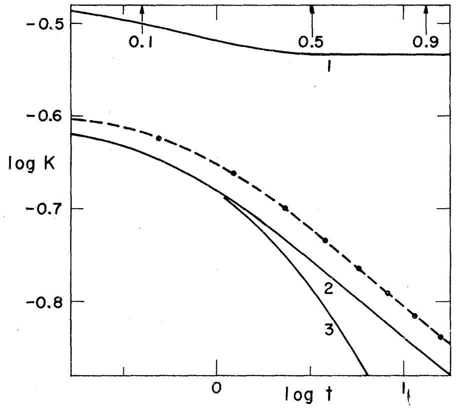

FIG. 1. Apparent first-order precipitation rate constant $K(t)$ vs t on logarithmic plot. The left and right margins are at the times for which 5% and 95%, respectively, of the impurity has precipitated, according to exact calculations for random sink distributions. Corresponding times for 10%, 50%, and 90% precipitation are also indicated. The dots and dashed line indicate exact results. Other curves show results for: (1) regular array of sinks, (2) isolated flux approximation, and (3) average t-matrix approximation. The density of sinks is $\rho=\frac{1}{4}$.

of sink locations. Fluctuations in $K(t)$ from one such array to another were largest at small densities and long times, where the maximum deviation in $\log_{10}K(t)$ from the average shown on the graph was ±0.05.

Results for the regular array of sink locations were obtained for a single sink on a lattice of sufficient size to give the correct ρ. Because of the periodic boundary conditions, the results must be the same for any square regular lattice of sinks with the same ρ. (This independence of size for regular arrays provided a check on programs designed for arbitrary arrays.)

For the isolated sink approximation $K(t)=\rho k(t)$, where $k(t)$ is the isolated sink flux, calculated from its Laplace transform $f(s)$ with $h(s)$ obtained from Eq. (2.18) with $l=1$. The average t-matrix results were obtained from Eq. (3.6).

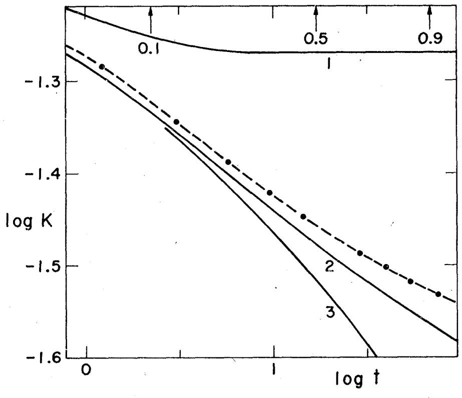

FIG. 2. See caption for Fig. 1. Here, $\rho=\frac{1}{16}$.

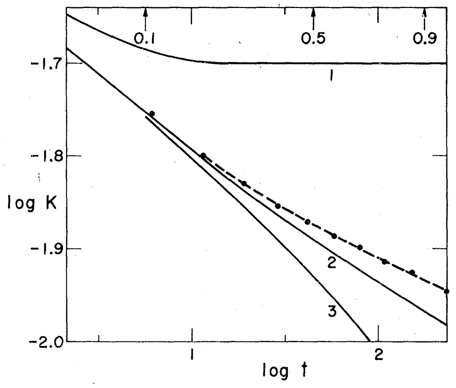

FIG. 3. See caption for Fig. 1. Here, $\rho=\frac{1}{36}$.

B. Discussion

It is apparent that the exact results for $K(t)$ show no sign of leveling off with increasing t, unlike the results for a regular lattice. Over the range of (5–95)% exhaustion of the impurity concentration, which is the range shown on the graphs, $K(t)$ drops rather steadily by an overall factor of roughly 2 for all densities considered.

Both approximations show the falloff of $K(t)$, but the equal flux approximation (alias the average t-matrix approximation), becomes quite poor at long times. The isolated flux approximation is still rather good at the longest times considered, and improves at short times as the concentration decreases. It would be interesting to improve the isolated sink approximation along the lines discussed in Sec. III. However, it seems possible (because of certain formal similarities to other percolation problems and polymer excluded volume problems), that the asymptotic kinetics as $t\rightarrow\infty$ may require more sophisticated approaches.

Experimental measurements on stress-assisted precipitation apparently show somewhat larger decreases of $K(t)$ than found here [the experiments were fit by Harper to a law $K(t)\propto t^{-1/3}$]. If the sinks were clustered, or alternatively, if the fluctuations of sink concentration were somewhat greater than random, a more rapid decrease of $K(t)$ would be found. This effect can be seen qualitatively from the approximation

$$C(t)\simeq\exp\left(-\rho\int_0^t k(t)\,dt\right).$$

An average over fluctuations in ρ favors the smaller ρ's more at longer times, and leads to a decrease in $-d\ \ln C(t)/dt$.

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