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The Kinetics of Adsorption to a One-Dimensional Lattice with Nearest-Neighbor Exclusion: A Series Expansion Study

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Exact 15-term series expansions are given for the cooperative kinetics of adsorption of particles to a one-dimensional lattice with nearest-neighbor exclusion. Padé approximants to various forms of the series accurately describe the relaxation process, which is found to be well-approximated by assuming instantaneous internal equilibrium on the lattice. The series do not describe the very last stages of decay to equilibrium well and it has not been possible to extract from them the limiting relaxation parameters. The series show that the rate of change of the particle density on the lattice is not analytic in the density when expanded about the equilibrium state.

KEY WORDS: Cooperative kinetics; time power series; radius of convergence; singularities.

1. INTRODUCTION

In the present paper I study the kinetics of adsorption of molecules from a reservoir of constant activity to a one-dimensional lattice with nearest-neighbor exclusion. This is one of the simplest models that one can construct to study the dynamics of cooperative condensation. Using matrix techniques derived from the statistical mechanics of two-dimensional equilibrium lattice gases, I obtain long (15-term) exact series expansions for the kinetics. I then compare the results of the series analysis with an exact solution obtained by assuming that the system passes through equilibrium states (internal equilibration) at all stages in the relaxation. I find that for the overall relaxation process the assumption of internal equilibration

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works quite well, but that when one examines the details of the final decay, the two approaches give very different pictures. I begin by describing the model.

2. THE MODEL

Consider a one-dimensional lattice initially in equilibrium with a reservoir containing the adsorbate at activity z_0; the lattice will have the same activity and an appropriate density $\rho_0(z_0)$. Throughout I assume that the reservoir and the lattice are homogeneous. At $t=0$ the activity of the reservoir is increased suddenly from z_0 to z_∞. The density of particles on the lattice will then increase, relaxing from $\rho_0(z_0)$ at $t=0$ to $\rho_\infty(z_\infty)$ at $t=\infty$. Figure 1 schematically illustrates the time dependence of the activity of the reservoir and the resultant relaxation of the lattice gas density. I consider only the special case $z_0=\rho_0=0$, i.e., I begin with an empty lattice. For simplicity I will use z to refer to the constant final activity of the reservoir when there is no danger of confusion.

In this model a particle can bind to a lattice site only if the nearest-neighbor lattice sites are empty. The model is illustrated in Fig. 2, where two processes are shown. The first process illustrated is exchange of particles between the reservoir and the lattice, a particle being able to bind to

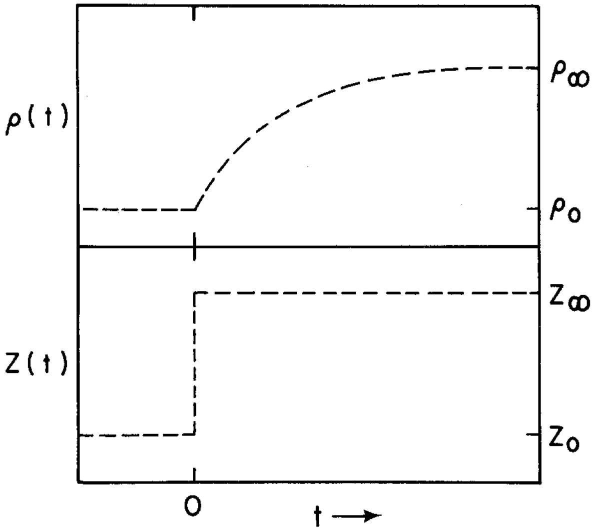

Fig. 1. Schematic representation of a step jump in the activity of the reservoir from z_0 to z_∞ at $t=0$ and the resulting relaxation of the density of particle ρ on the lattice from ρ_0 at $t=0$ to ρ_∞ at $t=\infty$.

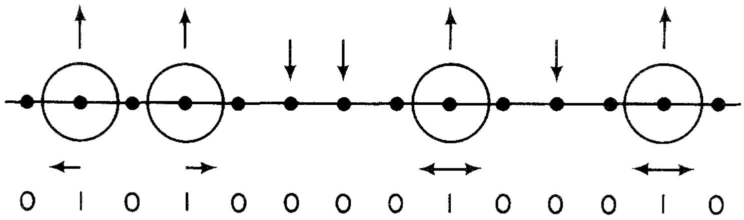

Fig. 2. Illustration of the 1D lattice gas with nearest-neighbor exclusion. The arrows represent the two possible types of process: the vertical arrows indicate exchange reactions with the reservoir, while the horizontal arrows represent diffusion on the lattice. The 1's and 0's index sites that are, respectively, occupied and vacant.

the lattice only if three contiguous sites are empty. The second process is the diffusion of particles on the lattice, a particle being able to move to a neighboring lattice site only if its two adjacent sites are unoccupied. Let us consider first the case where there is no diffusion on the lattice (exchange only).

Letting 0 and 1 represent, respectively, an empty and an occupied lattice site, then the basic mechanism for the change of density on the lattice will be the exchange of a particle with the reservoir, which I represent by the following reaction with forward (k^+) and backward (k^-) rate constants:

$$0 \underset{k^-}{\overset{k^+}{\longleftrightarrow}} 1 \tag{2.1}$$

From the principle of detailed balance one has

$$\begin{aligned} k^+/k^- &= z \qquad \text{(allowed transition)} \\ k^+/k^- &= 0 \qquad \text{(forbidden transition)} \end{aligned} \tag{2.2}$$

that is, a transition (addition of a particle) is either allowed or forbidden, and if it is allowed, a particle contributes a factor z to the probability of any lattice configuration. One could alternatively write $k^+/k^- = zK$, where K is the binding constant for the process of (2.1); this would simply scale the activity, $z' = zK$, and would not alter what follows. I choose

$$\begin{aligned} k^- &= 1 \\ k^+ &= z \qquad \text{(allowed transition)} \\ k^+ &= 0 \qquad \text{(forbidden transition)} \end{aligned} \tag{2.3}$$

as the simplest assignment that is consistent with the requirements of (2.2); any other choice, e.g., $k^- = 1/\sqrt{z}$ and $k^+ = \sqrt{z}$, simply redefines the time scale.

3. MATRIX GENERATION OF SERIES

The kinetics of adsorbtion for the model described in the previous section is determined by a set of coupled first-order differential equations describing the interconversion of all possible lattice configurations. Let $\mathbf{p}$ be a row vector whose general element p_n is the probability of the nth lattice configuration. Then the kinetics can be described by the equation

$$d\mathbf{p}/dt = -\mathbf{p}\mathbf{W} \tag{3.1}$$

where $\mathbf{W}$ is the appropriate matrix of rate parameters as given in (2.3). From (3.1) the nth derivative of $\mathbf{p}$ evaluated at $t = 0$ is

$$d^n\mathbf{p}/dt^n = (-1)^n\, \mathbf{p}(0)\, \mathbf{W}^n \tag{3.2}$$

Letting $\mathbf{v}^+$ be a column vector whose general element is the number of particles in the nth lattice configuration, one has a general relation for the net density

$$\rho(t) = \mathbf{p}(t) \cdot \mathbf{v}^+/N \tag{3.3}$$

where N is the number of sites in the lattice. Expanding $\rho(t)$ in a power series in the time

$$\rho(t) = \sum_{n=0}^{\infty} \rho^{(n)} t^n/n! \tag{3.4}$$

and using (3.2) and (3.3), one has

$$\rho^{(n)} = N^{-1}(-1)^n\, \mathbf{p}(0)\, \mathbf{W}^n \mathbf{v}^+ \tag{3.5}$$

The problem of course in using (3.5) is that as N, the number of lattice sites, is increased, the number of lattice configurations gets very large indeed. However, if one wraps the one-dimensional lattice into a circle, then one can use symmetry to greatly reduce the number of configurations that must be considered. The problem of the kinetics of the one-dimensional lattice with nearest-neighbor exclusion is in fact very similar to the equilibrium statistical mechanics of the two-dimensional lattice with nearest-neighbor exclusion. In the equilibrium problem the partition function for a lattice torus (consecutive rings of lattice sites) can be generated by a matrix that correlates all possible states of a single ring with all possible states of a neighboring ring (with the condition of nearest-neighbor exclusion). In the kinetic problem all of the states of a given ring can make appropriate transitions to other states of the ring. In both cases, the size of the required matrix is simply the number of ring configurations. Thus, the problem of obtaining time series for a one-dimensional model is equivalent in difficulty to obtaining the equilibrium activity series for a two-dimensional model, both being two-dimensional problems, the equilibrium problem having dimensions (space) × (space), while the kinetics problem has dimensions (space) × (time). For the equilibrium problem Runnels and Combs⁽¹⁾ have shown that one need consider only the irreducible set of ring configurations (those that cannot be obtained by reflection of rotation from the others).

To illustrate the use of symmetry-reduced matrices for kinetics, consider a ring of $N=4$ sites. There are three possible ring configurations in the irreducible set:

$$\begin{array}{ccc} \begin{array}{ccc} & 0 & \\ 0 & & 0 \\ & 1 & \end{array} & \begin{array}{ccc} & 1 & \\ 0 & & 0 \\ & 0 & \end{array} & \begin{array}{ccc} & 1 & \\ 0 & & 0 \\ & 1 & \end{array} \\ \\ (0) & (1) & (2) \end{array} \tag{3.6}$$

All other ring configurations can be obtained by rotations of configurations (1) and (2). The differential equations describing the kinetics are (where p_1 and p_2 represent the probabilities of the respective rings regardless of orientation)

$$\begin{aligned} dp_0/dt &= -4zp_0 + p_1 \\ dp_1/dt &= 4zp_0 - (1+z)\,p_1 + 2p_2 \\ dp_2/dt &= zp_1 - 2p_2 \end{aligned} \tag{3.7}$$

The appropriate matrix $\mathbf{W}$ is then

$$\mathbf{W} = \begin{pmatrix} 4z & -4z & 0 \\ -1 & 1+z & -z \\ 0 & -2 & 2 \end{pmatrix} \tag{3.8}$$

and the vectors $\mathbf{p}(0)$ and $\mathbf{v}^+$ are

$$\mathbf{p}(0) = (1\ \ 0\ \ 0), \qquad \mathbf{v}^+ = \begin{pmatrix} 0 \\ 1 \\ 2 \end{pmatrix} \tag{3.9}$$

As with the equilibrium system,$^{(2)}$ if one wants to obtain the $p^{(n)}$ in (3.4) through n for the infinite lattice, then one must consider a ring containing at least $n+1$ sites. Thus, to obtain through $\rho^{(15)}$ for the infinite lattice we require a ring with $n=16$; Runnels and Combs$^{(1)}$ have shown that the set of irreducible ring configurations in that case has 99 elements, requiring a 99×99 matrix. The $\rho^{(n)}$ generated from $\mathbf{W}^n$ will be polynomials in the activity

$$\rho^{(n)}=(-1)^n \sum_{m=0}^{n} \alpha_{mn} z^n \tag{3.10}$$

The α_{mn} for n through 15 are listed in Appendix A. The example treated above for $N=4$, using (3.8) and (3.9) in (3.5), gives the first three $\rho^{(n)}$ for the infinite lattice; these quantities are

$$\begin{gathered} \rho^{(1)}=z, \qquad \rho^{(2)}=-z-3z^2 \\ \rho^{(3)}=z+6z^2+11z^3 \end{gathered} \tag{3.11}$$

4. RADIUS OF CONVERGENCE

For any finite set of species connected by first-order reactions, such as (3.7), with the kinetics described by a differential equation of the form of (3.1), the exact solution is a sum of terms of the form $\exp(-\omega_i t)$, where the ω_i are the eigenvalues of the matrix $\mathbf{W}$. The series expansion (3.4) thus will have an infinite radius of convergence for a finite set of species, since the functions $\exp(-\omega_i t)$ converge for all t. However, in the limit that the number of species becomes infinite, the series can have a finite radius of convergence.

For a well-behaved series the easiest way to determine the radius of convergence is to examine the ratios of successive terms. Taking our basic series (3.4)

$$\begin{gathered} \rho(t)=\sum_n a_n t^n \\ a_n=\rho^{(n)}/n! \end{gathered} \tag{4.1}$$

we form the ratios

$$r_n=a_n/a_{n-1} \tag{4.2}$$

If the ratios vary smoothly with n, then one has

$$\lim n\to\infty, \qquad r_n\to t_\sigma^{-1} \tag{4.3}$$

where t_σ is the radius of convergence of the series. Figure 3 shows r_n as a function of $1/n$ constructed using the 15-term series of Appendix A; the case shown is for $z_\infty = 2$, in which case $\rho_\infty = 1/3$. The ratios are seen to vary monotonically with $1/n$, but they do not level off to a linear variation in the range shown. Clearly it is possible that the r_n could plunge to zero as $1/n \to 0$, but the variation of the r_n for the infinite lattice shown is very different in behavior from the r_n (not shown) for the finite ring $N = 4$, where the r_n obviously go to zero. If one takes successive pairs of points r_n and r_{n-1} and constructs a straight-line extrapolation for each pair, obtaining thereby a series of estimates $t_\sigma^{-1}(n)$, these extrapolate linearly with $1/n$ as shown in Fig. 3; the extrapolated value gives $t_\sigma^{-1} = 0.35$, or $t_\sigma = 2.86$. The straight line to which the r_n are shown approaching in Fig. 3 is the hypothetical variation of the ratios for a singularity of the form

$$[\rho_\infty - \rho(t)] \sim \left(\frac{1}{1 - t/t_\sigma}\right)^{\nu} \tag{4.4}$$

for which the ratios vary linearly with $1/n$ as(3)

$$r_n \sim t_s^{-1}[1 - (1/n)(1 - \nu)] \tag{4.5}$$

The line shown uses the parameters $t_\sigma^{-1} = 0.35$ and $\nu = 17$. There of course may be a more complicated form for the singularity than (4.4).

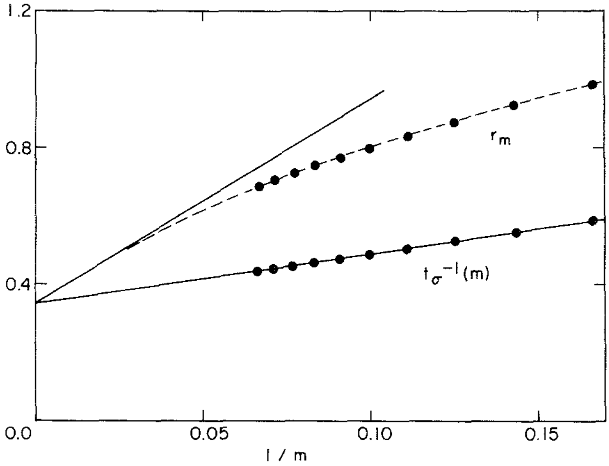

Fig. 3. Ratio r_m for the time series (4.1) for the case $z_\infty = 2$; the points shown are for $m = 6$ to 15. Also shown are the quantities $t_\sigma^{-1}(m)$ obtained from straight-line extrapolation of successive pairs of ratios to $1/m = 0$.

The evidence thus is strong that the time series for our one-dimensional hard-particle model has a singularity on the negative t axis and hence a finite radius of convergence. I speculate that this is a feature of all hard-particle systems, since it is found in the simplest such system.

Before turning to the numerical analysis of the series given in Appendix A, I will derive the kinetics of adsorption for the limit of internal equilibration which will be useful as a limiting case for comparison.

5. THE LIMIT OF INTERNAL EQUILIBRATION

The series derived in Section 3 describes the adsorption process when exchange with the reservoir is the only process allowed. As illustrated in Fig. 2, another possible process is the motion (diffusion) of particles on the lattice from one site to a neighboring site (if allowed). In the limit that the diffusion process is very much faster than the exchange process, one can consider the lattice to be in an instantaneous state of internal equilibrium appropriate to the particular density at a given time [the lattice is not in equilibrium with the reservoir, but is in internal equilibrium for the density $\rho(t)$ it has at a given instant of time]. In the limit of internal equilibration one can integrate the kinetic equations exactly and thereby obtain a limit that serves as a useful comparison for the case when diffusion is not allowed. It can be shown(4) that the case of internal equilibration is an upper bound for the rate of adsorption, that is, with diffusion the rate of adsorption must be faster than the case without diffusion.

The general differential equation for describing the adsorption kinetics, using the rate parameters of (2.3), for any hard-particle lattice gas is (here we let z_∞ be the activity of the reservoir, since we will have a time-dependent z for the lattice)

$$d\rho/dt = z_\infty \rho_x - \rho \tag{5.1}$$

where ρ_x is the density of sites that can accommodate a new particle (for the one-dimensional model with nearest-neighbor exclusion, $\rho_x = \rho_{000}$ where ρ_{000} is the probability of an unoccupied triplet). At equilibrium $d\rho/dt = 0$ and one has the well-known relation for hard-particle systems at activity z

$$\rho_x = \rho/z_\infty \tag{5.2}$$

In the limit of internal equilibration (5.2) holds at all densities, thus defining a time-dependent activity z. Using (5.2) in (5.1) gives

$$\frac{d\rho}{dt} = \left(\frac{z_\infty}{z} - 1\right)\rho \tag{5.3}$$

To use (5.3) one requires the equilibrium relationship between z and ρ so that one can obtain a differential equation solely in terms of ρ (and t). To this end let us construct the grand partition function for the one-dimensional lattice of N sites with periodic boundary conditions (i.e., a ring of sites), which can be expressed as the trace of a matrix product as follows$^{(5)}$:

$$\Xi = \operatorname{Tr} \mathbf{U}^N \to \lambda_1^N \qquad (N \to \infty) \tag{5.4}$$

where λ_1 is the largest eigenvalue of the transition matrix $\mathbf{U}$, which is simply

$$\mathbf{U} = \begin{array}{c|cc} & 0 & 1 \\ \hline 0 & 1 & 1 \\ 1 & z & 0 \end{array} \tag{5.5}$$

The density is obtained from λ_1 in the usual manner,

$$\rho = \frac{\partial \ln \lambda_1}{\partial \ln z} = \frac{1}{2}\left(1 - \frac{1}{(1+4z)^{1/2}}\right) \tag{5.6}$$

One obtains

$$\frac{\rho}{z} = \frac{(1-2\rho)^2}{1-\rho} \tag{5.7}$$

Using (5.7) in (5.3), one has the following differential equation for ρ:

$$\frac{d\rho}{dt} = z_\infty \frac{(1-2\rho)^2}{1-\rho} - \rho \tag{5.8}$$

which is readily integrated to give

$$\frac{\rho_\infty - \rho}{\rho_\infty - \rho_0}\left(\frac{1-\rho_\infty-\rho_0}{1-\rho_\infty-\rho}\right)^\beta = e^{-t/\tau} \tag{5.9}$$

where

$$\beta = \rho_\infty/(1-\rho_\infty), \qquad \tau = 1 - 3\rho_\infty + 2\rho_\infty^2 \tag{5.10}$$

The quantity ρ_∞ as a function of z_∞ is obtained from (5.6).

For the special case $z_\infty = 2$ and $\rho_0 = 0$ (with $\rho_\infty = 1/3$, $\beta = 1/2$, and $\tau = 2/9$), (5.9) can be solved explicitly for $\rho(t)$,

$$\rho(t) = \frac{1}{3} - \frac{1}{3\sqrt{2}} e^{-9t/2}\left(1 + \frac{1}{8} e^{-9t}\right)^{1/2} + \frac{1}{12} e^{-9t} \tag{5.11}$$

6. PADÉ APPROXIMANTS TO TIME SERIES

Given a finite number of terms in a time series such as (3.4) or (4.1), there are two practical problems in the use of such a series. One is to estimate the complete function by extrapolating the series to an infinite number of terms and the second is to extend the series past its radius of convergence. The technique of Padé approximants offers a solution to both of these problems.(6) Given $M+N$ terms in (3.4), the (M, N) Padé approximant is

$$\rho(t) \cong P(M, N) = \sum_{m=0}^{M} A_m t^m \bigg/ \sum_{m=0}^{N} B_m t^m$$
$$= \sum_{n=0}^{M+N} a_n t^n + \sum_{n=M+N+1}^{\infty} a'_n t^n \tag{6.1}$$

where the a_n are the known exact coefficients in the series and a'_n are estimates of the remaining coefficients. The finite ratio of polynomials in (6.1) gives an analytic continuation of the series past the radius of convergence $|t_\sigma|$.

In general we have found that the diagonal, $M=N$, Padé approximants work best for time series (the diagonal approximants approach a finite limit as $t \to \infty$). Figure 4 shows $P(N, N)$ for $N=1$, $N=2$,

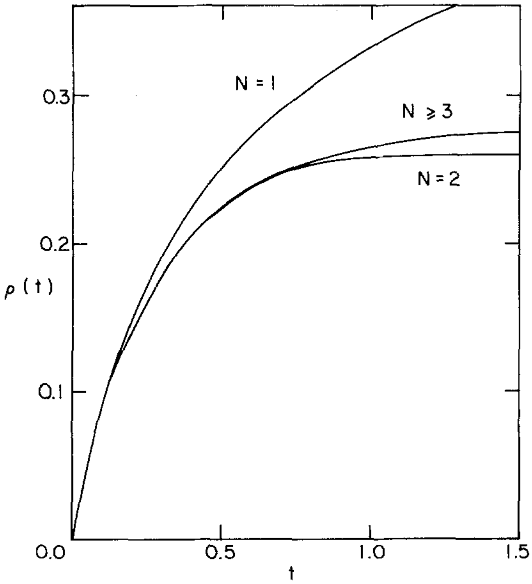

Fig. 4. The (N, N) Padé approximants to $\rho(t)$ for the case $z_\infty = 1$.

and $N \geqslant 3$ (which are superimposable) for the case $z_\infty = 1$ ($\rho_\infty = 0.276$). One observes that the ratio of polynomials levels off and holds constant at the correct value of ρ_∞; note that the value of ρ_∞ was not used directly. Figure 5 shows the $P(5, 5)$ estimate of $\rho(t)$ for $z_\infty = 1/2$, 1, and 2 ($\rho_\infty = 0.211$, 0.276, and 0.333, respectively). Again the curves level off and hold constant at the correct value of ρ_∞.

For the case of $z_\infty = 2$, Fig. 5 compares $P(N, N)$ for the case of exchange only and the case of internal equilibration, (5.11), the latter shown by the dashed line. One sees that there is very little difference between the two relaxation curves, meaning that internal diffusion does not influence the time course of relaxation markedly for this model. For $z_\infty = 1/2$ and $z_\infty = 1$ one can see no difference in the two cases on the scale of the graph in Fig. 5.

One can conclude two things from the data just presented. First, the technique of Padé approximants applied directly to finite time series for $\rho(t)$ works extremely well, giving the complete relaxation to the final equilibrium state. Second, the limit of internal equilibration is not only an upper bound to the rate of relaxation in this model, it is an extremely good estimate of the relaxation for all times.

And yet, if one examines in detail the nature of $\rho(t)$ as $t \to \infty$, one finds both quantitative and qualitative differences between the limit of

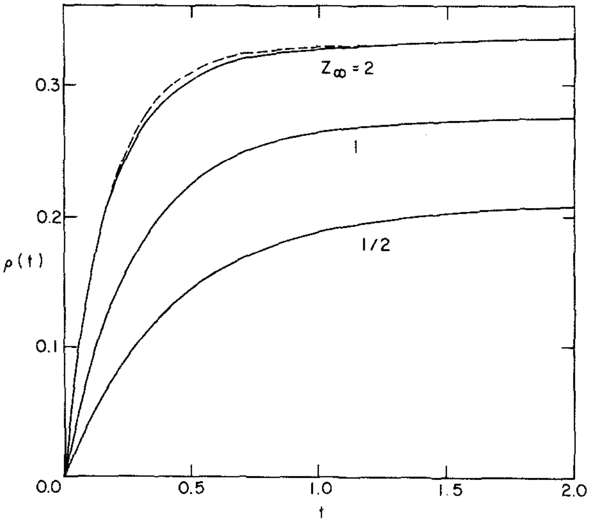

Fig. 5. The (5, 5) Padé approximants (solid curves) to $\rho(t)$ for $z_\infty = 1/2$, 1, and 2. The dashed curve gives $\rho(t)$ in the limit of internal equilibration for $z_\infty = 2$ obtained from (5.11); for the other values of z_∞ the limits of internal equilibration and exchange only are indistinguishable on the scale of this graph.

internal equilibration and the case of exchange only. From the close agreement of the two curves in Fig. 5 it is clear that this difference would not be apparent from an experimental curve or from a Monte Carlo computer simulation. But it does become apparent when one has long (15 terms in this case) exact series. I now examine the differences in the two limits (exchange only and internal equilibration) in detail.

7. RELAXATION FUNCTION AND EULER TRANSFORM

It is convenient to introduce a function that varies from one to zero over the course of the adsorption process. This is easily accomplished by introducing the function

$$\Delta = 1 - \rho/\rho_\infty \tag{7.1}$$

which has the properties

$$\Delta(t=0) = 1, \qquad \Delta(t=\infty) = 0 \tag{7.2}$$

Since all relaxation curves look qualitatively similar, it is also useful to introduce a function that measures how Δ differs from the simplest form of relaxation, namely simple exponential decay. Define the relaxation function $k(t)$ by the relation

$$\Delta(t) = e^{-tk(t)} \tag{7.3}$$

where $k(t)$ is a kind of time-dependent relaxation parameter. If Δ represents simple exponential decay, then $k(t)$ would be a constant. If $k(t)$ decreases with time, then it means that the process is slowing down relative to simple decay, and vice versa.

Finally, it simplifies matters if one defines the time scale so that $k(t=0) = 1$. This is achieved by scaling t as follows:

$$t' = \frac{z_\infty}{\rho_\infty} t \tag{7.4}$$

Using (7.1) and (7.4), the $\rho^{(n)}$ of (3.4) are scaled to give

$$\rho^{(n)'} = \rho_\infty \left(\frac{z_\infty}{\rho_\infty}\right)^n \rho^{(n)} \tag{7.5}$$

For simplicity I will drop the prime on t and understand that for the rest of this paper the scaled variable of (7.4) is being used.

Since we will be interested in the behavior of the relaxation as $t \to \infty$, it is useful to map the interval $t=0$ to $t=\infty$ onto the unit line. This is accomplished by using the Euler transform

$$s=\frac{t}{1+t}, \qquad t=\frac{s}{1-s}$$
$$s(t=0)=0, \qquad s(t=\infty)=1 \tag{7.6}$$

Not only is s a convenient variable, but the use of s circumvents the problem associated with a finite radius of convergence in the t series, since a negative t_σ is mapped to a positive s_σ with $s_\sigma>1$ and hence the s series converges over the entire physical range of the function.

Combining the $k(t)$ function introduced in (7.3) and the new variable s defined in (7.6) gives

$$\Delta(s)=\exp\left[-\left(\frac{s}{1-s}\right)k(s)\right] \tag{7.7}$$

For the case $z_\infty=2$ the function $k(s)$ is shown in Fig. 6 for the case of exchange only [labeled $\xi=0$, where ξ is a parameter measuring the rate of diffusion; see (9.1)] and, using (5.11), for the case of internal equilibration

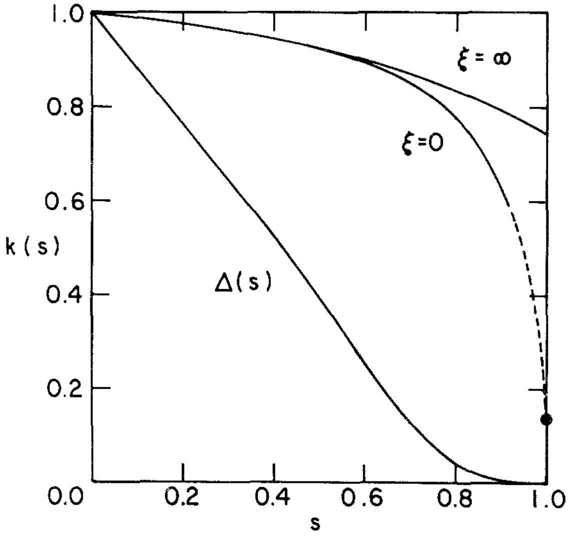

Fig. 6. Variation of the relaxation function $k(s)$ as defined by (7.7) and (7.6) for the case $z_\infty=2$ for $\xi=0$ (exchange only) and $\xi=\infty$ (internal equilibration). For comparison $\Delta(s)$ is also shown for the case $\xi=0$. The solid dot at $s=1$ for the $\xi=0$ $k(s)$ function is taken from Fig. 7. The curve for $\xi=\infty$ is obtained from (5.11); the curve for $\xi=0$ (solid curve) is the (7, 7) Padé approximant to $k(s)$.

($\xi = \infty$). For the case of internal equilibration $k(s)$ varies from $k(0) = 1$ to $k(1) = 3/4$. The curve for exchange only was calculated using Padé approximants to the $k(s)$ series, which in turn were constructed from the t series of Appendix A; the curve is shown with a solid line out to about $s = 0.9$, at which point one begins to get disagreement among the various approximants. One sees that the $k(s)$ curves for the two limits are almost superimposable up to about $s = 0.5$; for $s > 0.5$ the curves begin to diverge markedly. From the practical point of view, most of the relaxation is over with by $s \approx 0.6$ and hence, as seen in Fig. 5, the overall relaxation curves $\Delta(s)$ are very similar in the two limits. Only in the last stages of the relaxation process do the $k(s)$ curves begin to diverge. For comparison the variation of $\Delta(s)$ is shown for the case of exchange only.

In the case of exchange only the crucial question is whether $k(1)$ approaches a finite limit or drops to zero. Since the series for $k(s)$ are not adequate to give reliable estimates of $k(s)$ for $s > 0.9$, we have estimated $k(1)$ by calculating the eigenvalue spectrum for various finite rings containing from $N = 2$ up to $N = 16$ lattice sites. Figure 7 shows the smallest eigenvalue ω_0 plotted as a function of $2/N$ for the case of $z_\infty = 2$; the units are such that $k(0) = 1$. The quantity ω_0 seems clearly to extrapolate to a finite limit as $N \to \infty$; we estimate the limiting value to be $\omega_0 = 0.134$. The point $\omega_0 = 0.134 = k(1)$ is shown by the solid dot as $s = 1$ in Fig. 6; the dashed

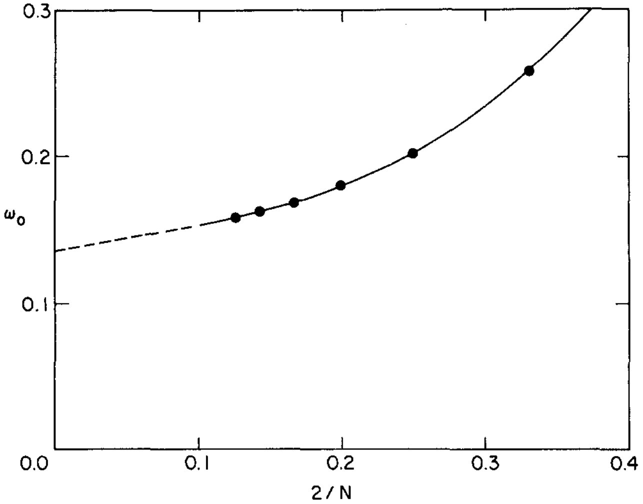

Fig. 7. The points show the smallest finite eigenvalue ω_0 for finite rings of N sites for the 1D lattice gas with nearest-neighbor exclusion for $z_\infty = 2$ and $\xi = 0$. The dashed curve is the extrapolation to the infinite system. The units are such that $k(0) = 1$.

curve is a freehand interpolation between the Padé approximant calculation of $k(s)$ (solid curve) and the point ω_0.

Thus, while the $k(s)$ curves for the limits of exchange only and internal equilibration agree well for $s<0.5$, they diverge markedly as $s\to 1$. For exchange only $k(s)$ appears to approach the point $k(1)$ with a slope of minus infinity. This is the behavior one would expect for the asymptotic form

$$\Delta(t)\sim\frac{a}{t^{\nu}}e^{-\omega_0 t} \tag{7.8}$$

In the next section I analyze various series to see if the form of (7.8) can be confirmed.

8. SEARCH FOR SINGULARITIES

It is useful to list and tabulate the various functions that we can use. Let us continue to examine the case $z_\infty=2$ with $\rho_\infty=1/3$ treated in the previous sections and illustrated in Figs. 5–7. Let us use the scaled time defined in (7.4) and the variable ρ/ρ_∞. The functions that we will study are

$$\rho/\rho_\infty=\sum_n a_n t^n \tag{8.1}$$

$$t=\sum_n b_n(\rho/\rho_\infty)^n \tag{8.2}$$

$$d(\rho/\rho_\infty)/dt=\sum_n c_n(\rho/\rho_\infty)^n \tag{8.3}$$

$$k(s)=\sum_n d_n s^n \tag{8.4}$$

The coefficients in the above series are listed in Table I.

The coefficients in (8.1) alternate regularly; in Section 4 we have already examined the ratios for this series and have shown that the evidence is good that there is a singularity on the negative t axis [at $t_\sigma=-17.14$, using the time units of (7.4)]. If we invert (8.1), we obtain t as a function of ρ. All of the coefficients in (8.2) are positive and this is what one would expect, since $t\to\infty$ as $\rho\to\rho_\infty$. In fact, given a finite ω_0, we know how t goes to infinity at ρ_∞ since, even with the form of (7.8),

$$\begin{aligned}\ln\Delta &\sim \ln a-\nu\ln t-\omega_0 t\\ &\sim -\omega_0 t\left(1-\frac{\ln a}{\omega_0 t}-\frac{\nu\ln t}{\omega_0 t}\right)\\ &\sim -\omega_0 t\end{aligned} \tag{8.5}$$

Table I. The Coefficients in the Series Defined in Eqs. (8.1)–(8.4)[a]

n	a_n of (8.1)	b_n of (8.2)	c_n of (8.3)	d_n of (8.4)
0	0	0	1	1
1	1	1	−1.17	−0.0833
2	−0.583	0.583	0.111	−0.0694
3	0.264	0.417	0.0247	−0.0581
4	−0.103	0.326	9.26(−3)	−0.0489
5	0.0366	0.269	4.60(−3)	−0.0417
6	−0.0120	0.230	2.72(−3)	−0.0363
7	3.70(−3)	0.201	1.81(−3)	−0.0323
8	−1.08(−3)	0.179	1.30(−3)	−0.0295
9	3.00(−4)	0.162	9.85(−4)	−0.0279
10	−7.99(−5)	0.148	7.79(−4)	−0.0271
11	2.05(−5)	0.136	6.35(−4)	−0.0271
12	−5.09(−6)	0.126	5.30(−4)	−0.0277
13	1.23(−6)	0.118	4.51(−4)	−0.0288
14	−2.87(−7)	0.111	3.89(−4)	−0.0303
15	6.57(−8)	0.104		

[a] The time is scaled according to (7.4); the density is written as (ρ/ρ_∞). The coefficients are given for the case $z_\infty = 2$ with $\rho_\infty = 1/3$. The coefficients are shown to three figures only for clarity; the numbers in parentheses give the number m in the factor 10^m by which the particular coefficient should be multiplied.

that is, if ω_0 is finite, then

$$\begin{aligned} t &\sim -(1/\omega_0)\ln \Delta \\ &\sim -(1/\omega_0)\ln(1-\rho/\rho_\infty) \end{aligned} \tag{8.6}$$

Taking the derivative of t with respect to ρ/ρ_∞, one has the useful form

$$\frac{dt}{d(\rho/\rho_\infty)} \sim \frac{1}{\omega_0}\left(\frac{1}{1-\rho/\rho_\infty}\right) \tag{8.7}$$

Using the b_n of (8.2) in (8.7), one has

$$\omega_0 \sim 1/nb_n \tag{8.8}$$

Thus, the sequence of numbers $(nb_n)^{-1}$ should approach ω_0 as a limiting value. The estimates of ω_0 obtained from the b_n of Table I are shown in Table II. While the results do seem to settle down to a limit, it is not the ω_0 (0.134) obtained from Fig. 7 by extrapolation using finite rings. To investigate the rate of convergence of (8.8) to a limiting value, I have also computed the $(nb_n)^{-1}$ for the case of the finite ring $N = 4$; these numbers are also shown in Table II. The exact value of ω_0 for the finite ring is $\omega_0 = 0.6402$ and the numbers $(nb_n)^{-1}$ are seen to converge quickly to the near neighborhood of this number (with about a 5% tendency to wander a bit). The problem is that the $(nb_n)^{-1}$ for the case of the infinite ring do not differ that much from the values for the case of the finite ring (as shown in Section 9, the first three terms in the series in the two cases are identical). Accepting the value of ω_0 obtained from Fig. 7, this means that the shift of $(nb_n)^{-1}$ to $\omega_0 = 0.134$ must occur at very large values of n; this simply means that for most of the relaxation, $\Delta(s)$ is described accurately by the limit of internal equilibration (for which $\omega_0 = 3/4$ in this case).

It is the density series for $d(\rho/\rho_\infty)/dt$, (8.3), that tells us the most about the functional form at long times. As we have just seen, the ρ series of (8.2) will diverge as $\rho \to \rho_\infty$. This will be true for any kinetic scheme, even simple chemical kinetics including a single first-order decay, and the reason is of course that as $\rho \to \rho_\infty$, t must go to infinity. Thus, it might seem that the ρ series in (8.3) would also diverge as $\rho \to \rho_\infty$, since, after all, the series in (8.2) and (8.3) are both derived from (8.1). But in ordinary chemical kinetics the ρ dependence of $d(\rho/\rho_\infty)/dt$ is a finite polynomial (e.g., linear or quadratic). In the limit of internal equilibration we can see immediately from (5.8) that the radius of convergence of $d(\rho/\rho_\infty)/dt$ is

Table II. Successive Ratios of Coefficients in the Density Series (8.2) and (8.3)[a]

n	b_{n-1}/b_n	c_{n-1}/c_n
2	1.72	
3	1.40	4.49
4	1.28	2.68
5	1.21	2.01
6	1.17	1.69
7	1.14	1.50
8	1.12	1.39
9	1.10	1.32
10	1.09	1.26
11	1.09	1.23
12	1.08	1.20
13	1.07	1.18
14	1.06	1.16
15	1.06	

[a] In both cases the ratios should be asymptotic to ρ_σ/ρ_∞, where ρ_σ is the radius of convergence of the series. For both series the ratios approach unity, which means that for both the radius of convergence is $\rho_\sigma = \rho_\infty$.

$\rho_\sigma = 1$, which is twice the maximum possible density ($\rho_{\max} = 1/2$) and much greater than ρ_∞. For the case of exchange only we can apply the ratio method, (4.2), to (8.3) and obtain successive estimates of $\rho_\sigma t(\rho/\rho_\infty)$ and for $d(\rho/\rho_\infty)/dt$,

$$\lim n \to \infty : b_{n-1}/b_n \sim (\rho_\sigma/\rho_\infty), \qquad c_{n-1}/c_n \sim (\rho_\sigma/\rho_\infty) \tag{8.9}$$

The values of b_{n-1}/b_n and c_{n-1}/c_n are shown in Table II; both of these sequences of numbers clearly extrapolate to $\rho_\sigma/\rho_\infty = 1$, which means that the radius of convergence for both series is $\rho_\sigma = \rho_\infty$. The ratios $r_n = c_n/c_{n-1}$ as in (4.2), for the ρ series for $d\rho/dt$ [(8.3), but not scaled by ρ_∞] are shown in Fig. 8 for the cases $z_\infty = 1/2$, 1, and 2; the ratios are seen to extrapolate smoothly to the appropriate values of ρ_∞^{-1}. This means that for the case of exchange only, unlike the case of internal equilibration, the radius of convergence of the ρ series for $d\rho/dt$ is the final density. And this has a very important implication. It means that one cannot expand $d\Delta/dt$ about the final, equilibrium state; that is, the series

$$\frac{d\Delta}{dt} = \sum_n C_n \Delta^n \tag{8.10}$$

does not exist.

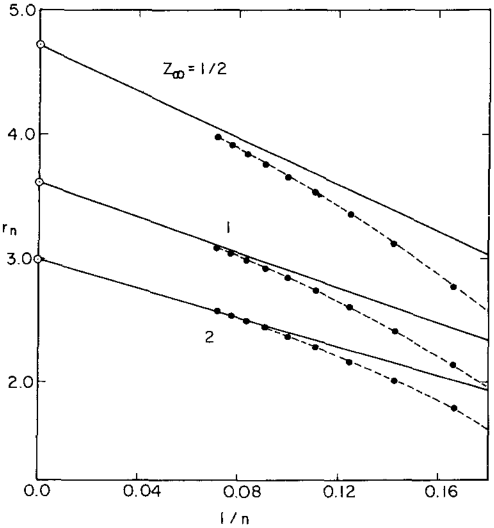

Fig. 8. Ratio r_n for the density series (8.3) for several values of z_∞. The points given are for $n=7$ to 15. The open circles at $1/n=0$ are the values of ρ_∞^{-1} corresponding to the values of z_∞ indicated. The straight lines are just guides for the eye.

If $\Delta(t)$ behaved asymptotically at large t as given by (7.8), then one would have

$$\frac{d\Delta}{dt} \sim -\omega_0 \Delta - \nu\omega_0 \frac{\Delta}{\ln \Delta} \tag{8.11}$$

This means that the term linear in Δ is finite, but the series in higher powers of Δ does not exist. Thus, from (8.3) one can form (using $\Delta = 1 - \rho/\rho_\infty$) the zeroth- and first-order terms in $d\Delta/dt$,

$$\frac{d\Delta}{dt} = -\left(\sum_{n=0}^{\infty} c_n\right) - \left(\sum_{n=1}^{\infty} nc_n\right)\Delta + f(\Delta) \tag{8.12}$$

where $f(\Delta)$ cannot be expressed as a series expansion in Δ. From (8.10) we expect

$$\sum_{n=0}^{\infty} c_n = 0 \qquad -\sum_{n=1}^{\infty} nc_n = \omega_0 \tag{8.13}$$

Table III shows the partial sums

$$S_n = \sum_{m=0}^{n} mc_m \tag{8.14}$$

as successive estimates of ω_0. For the case of the finite ring the partial sums converge nicely to the known imit, $\omega_0 = 0.6402$, but the numbers for the infinite ring are very far from the value of $\omega_0 = 0.134$ obtained from Fig. 7. Again, it seems that the series for the infinite system converge very slowly indeed.

The quantities c_n are themselves functions of ρ_∞. The question of forming a series in ρ_∞ for ω_0 is addressed in Appendix B.

If the form of (7.8) is correct, then one should have [from (8.10)]

$$\frac{d(\rho/\rho_\infty)}{dt} \sim \nu\omega_0 \frac{1 - \rho/\rho_\infty}{\ln(1 - \rho/\rho_\infty)} \tag{8.15}$$

The series expansion for the function

$$f(x) = \frac{-(1-x)}{\ln(1-x)} = \frac{1}{x} \sum_{n=0}^{\infty} \gamma_n x^n \tag{8.16}$$

is readily calculated numerically. One then has

$$\nu\omega_0 \sim c_n/\gamma_{n+1} \tag{8.17}$$

Table III. Estimates of the Parameters v and ω_0 Using the Series (8.2) and (8.3)[a]

	Infinite ring		Finite ring		
n	$\omega_0(n)$	S_n	$\omega_0(n)$	S_n	c_n/γ_{n+1}
1	1.000	1.167	1.000	1.235	
2	0.857	0.944	0.810	0.986	2.67
3	0.800	0.870	0.714	0.810	1.62
4	0.767	0.833	0.658	0.686	1.21
5	0.744	0.810	0.626	0.602	1.03
6	0.726	0.794	0.607	0.550	0.937
7	0.711	0.781	0.597	0.522	0.898
8	0.699	0.771	0.594	0.512	0.886
9	0.688	0.762	0.595	0.514	0.890
10	0.678	0.754	0.599	0.525	0.904
11	0.669	0.747	0.604	0.541	0.924
12	0.660	0.741	0.610	0.559	0.948
13	0.652	0.735	0.617	0.557	0.975
14	0.645	0.730	0.623	0.594	1.003
15	0.638		0.628	0.608	
16			0.633	0.620	
17			0.636	0.630	
18			0.639	0.637	
19			0.641	0.641	

[a] The quantities shown are $\omega_0(n) = (nb_n)^{-1}$ and the partial sequences S_n defined by (8.14), which are tabulated for the infinite ring using the data of Appendix A and, for comparison, for the finite ring with $N=4$ calculated using the matrix of (3.8). Even though the coefficients $\rho^{(n)}$ through $n=3$ are identical for the $N=4$ and the $N=\infty$ cases, the quantities $\omega_0(n)$ and S_n differ through $n=3$, since the value of ρ_∞ used in the two cases is different: $z_\infty = 2$ for both, $\rho_\infty(N=\infty) = 1/3$, $\rho_\infty(N=4) = 0.353$. The quantity c_n/γ_{n+1}, which is asymptotic to $v\omega_0$, is also shown for the infinite lattice; the γ_n are the coefficients in (8.16).

The values of the terms c_n/γ_{n+1} are listed in Table III; this quantity is seen to rapidly approach an approximately constant value, supporting the form or (8.13) or (8.10) [and hence of (7.8)]. The successive estimates of $v\omega_0$ seem to be approaching a limit that is approximately one; thus, $v \approx \omega_0^{-1}$.

Finally, let us examine the $k(s)$ series of (8.4). From Table I the series is seen to be well behaved, the coefficients beyond the first few terms being almost constant; if that behavior continues, then $k \rightarrow -\infty$ as $s \rightarrow 1$. Clearly the terms we are seeing in Table I are responsible for the final plunge that the function $k(s)$ takes as $s \rightarrow 1$. However, the function does not plunge to $-\infty$, but stops at ω_0, probably with an infinite slope; this behavior must be reflected in further terms in the series. Clearly, the estimate of the limiting value of $k(s=1)$ from the series

$$\omega_0 = k(s=1) = \sum_{n=0}^{\infty} d_n \tag{8.18}$$

will not work, even though the s-series should converge at $s=1$; we simply do not have enough terms.

If the form of (7.8) is correct, then $k(s)$ should have the following asymptotic form:

$$k(s) \sim \omega_0 - \nu \left(\frac{1-s}{s}\right) \ln \frac{1-s}{s} \tag{8.19}$$

and

$$\frac{d^2k}{ds^2} \sim \frac{\nu}{1-s} \tag{8.20}$$

Equation (8.20) tells us that if we form the series d^2k/ds^2 and remove a simple pole, we can obtain ν as the residue (e.g., by using Padé approximants); in a similar manner one can obtain ω_0 as the residue of a simple pole using (8.7). From the behavior of the coefficients d_n in Table I, $k(s)$ itself is behaving as if it has a simple pole at $s=1$ ($k \to -\infty$ as $s \to 1$), and hence (8.19) clearly will not work with the series we have. The approach os using (8.20) is, however, attractive, since it gives an estimate of ν independent of ω_0.

Equation (8.19) implies that if one plots $k(s)$ as a function of $x \ln x$, where $x=(1-s)/s$, one should get a straight line with intercept ω_0 and slope ν. Taking the data for $k(s)$ from the solid-line Padé approximant shown in Fig. 6, one can fit the data to a straight line terminating in $\omega_0 = 0.134$. The value of ν so obtained is $\nu \approx 1.9 \pm 0.1$, the error indicating the uncertainty in the data. Since this procedure uses data only up to $s=0.9$ and since we have seen that the series are very slow to converge, one must be skeptical of the accuracy of this number. This number is consistent with the estimate of $\nu\omega_0 \approx 1$ obtained from (8.17) if one uses the value $\omega_0 \approx 0.6$ (rather than 0.134) obtained from the numbers in Table III.

9. SERIES INCLUDING DIFFUSION

Up to now we have treated series for the exchange-only mechanism. Diffusion on the surface was included only in the limit of internal equilibration (diffusion much faster than exchange). In this section I illustrate how a finite rate of surface diffusion can be included in the series expansions. Let ξ represent the rate parameter for the hopping of a particle from a general site to a neighboring site (if such a move is allowed by our occupancy rules, i.e., nearest neighbor exclusion)

$$00\underline{110}00 \xleftrightarrow[\xi]{\xi} 00\underline{01}00 \tag{9.1}$$

where the sites involved in the switch have been underlined. Let ξ be the rate parameter for the reaction in both directions (of course if the reaction is forbidden, the rate parameter is zero). Incorporating the effect of the appropriate diffusion reactions between the various ring configurations into the series is accomplished by including these reactions into the matrix **W** of (3.5). The coefficients $\rho^{(n)}$ are now functions of z (shorthand for z_∞) and ξ. I have determined the $\rho^{(n)}$ through $n = 6$ to see how the influence of internal diffusion enters the problem:

$$\begin{aligned}
&\rho^{(0)} = 0, \qquad \rho^{(1)} = z, \qquad -\rho^{(2)} = z + 3z^2 \\
&\rho^{(3)} = z + 6z^2 + 11z^3 \\
&-\rho^{(4)} = z + 9z^2 + 35z^3 + 47[45]\, z^4 \\
&\rho^{(5)} = z + 12z^2 + 26z^3 + (216 + 4\xi)[198]\, z^4 + 227[193]\, z^5 \\
&-\rho^{(6)} = z + 15z^2 + 142z^3 + (646 + 44\xi + 16\xi^2)[546]\, z^4 \\
&\qquad + (1413 + 68\xi)[1057]\, z^5 + 1215[819]\, z^6
\end{aligned} \tag{9.2}$$

Setting $\xi = 0$ gives the series given in Appendix A. The numbers in square brackets are the values of the coefficient of z^k in the limit $\xi \to \infty$ (internal equilibration). Obviously one cannot simply set $\xi = \infty$ in (8.2); the relation between the $\rho^{(n)}$ for finite and infinite ξ is discussed in Appendix C.

One sees in (9.2) that with the initial condition $\rho^{(0)} = 0$ (empty lattice at $t = 0$), the influence of internal diffusion first appears in $\rho^{(5)}$, but that in the limit $\xi \to \infty$, $\rho^{(4)}$ is altered (see Appendix C). The fact that internal diffusion has a very small effect on the early terms in the series presumably is the reason that the various series expansions examined in the previous section converge so slowly to give accurate estimates of ω_0 and v.

10. DISCUSSION

As mentioned in Section 3, the task of obtaining series expansions for the kinetics of one-dimensional models is equivalent in difficulty to obtaining the series for the equilibrium properties of two-dimensional models.

Thus, it will be extremely difficult to obtain much longer series expansions for cooperative kinetics than the series reported here. A few one-dimensional cooperative kinetic models have been solved exactly, the most notable example being the kinetic Ising model of Glauber,(7) which can be interpreted as a one-dimensional adsorption model with attractive nearest-neighbor interactions and a special choice of the rate parameters. In that model Glauber finds that the exact solution is simple exponential decay. Since the kinetics in the present model is much more complicated than that, I speculate that the effect of repulsion alone always leads to more complicated kinetics than does attraction alone. Evans *et al.*(8) have studied the irreversible filling of lattices with steric hindrance; the present model treats the reversible filling, allowing the particles on the lattice to ultimately come to equilibrium. My purpose in carrying out the present study was to see how much information could be extracted from series solutions and how good the approximation of internal equilibration is.

From the practical point of view, that is, in obtaining the overall relaxation, e.g., as described by $\Delta(s)$ in (7.7), the series work very well. As shown in Fig. 6, Padé approximants to $k(s)$ give a very accurate description of $k(s)$ out to about $s = 0.9$ (recall that $s = 1$ corresponds to $t = \infty$); as seen in Fig. 6, $\Delta(s)$ has dropped essentially to zero well before the point $s = 0.9$ is reached. In addition, we have seen that the approximation of internal equilibration is quite good over almost the whole course of the relaxation, as shown by the close agreement of the curves for $k(s)$ in the limits of exchange only and internal equilibration for $s < 0.5$.

From the point of view of describing accurately the very last stages of the relaxation, the series do not work well at all. None of the various methods used here comes close to giving the correct estimate of $\omega_0 = k(1)$ obtained from the numerical extrapolation of the smallest eigenvalue for finite rings (shown in Fig. 7). Clearly this means that when one has exchange only, the shifting of particles on the surface to make room for the last particles is very slow when one has to desorb and readsorb to move a particle (rather than moving by surface diffusion). This means that series expansions for more complicated one-dimensional and higher-dimensional systems (where it will be more difficult to obtain series of comparable length to those used in the present study) will probably not be useful to obtain asymptotic relaxation parameters. This is in contrast to the behavior of the Glauber(7) model with attractive nearest-neighbor interactions (in the adsorption model interpretation), where the decay is exactly simple exponential decay and the coefficient of the linear term in the density expansion of $d\rho/dt$ gives the exact behavior for all time!

The most important finding of this study is that the radius of convergence of the $d\rho/dt$ series as a function of ρ is ρ_∞, which means that a series expansion about the equilibrium state does not exist beyond the linear term. Thus, one can linearize the kinetics of such cooperative systems about the equilibrium state, but one cannot systematicaly move on and obtain the quadratic term and so on; one must know the nature of the long-time functional form [e.g., (7.8) for the present model]. I speculate that this will be a property of all cooperative models that include a hard-core, repulsive part in the interaction potential.

APPENDIX A

In this Appendix I give the coefficients $\rho^{(n)}$ in the series

$$\rho(t) = \sum_{n=0}^{\infty} \rho^{(n)} t^n / n! \tag{A.1}$$

for the model of reversible adsorption from a reservoir to a linear lattice with nearest-neighbor exclusion discussed in the text. The coefficients $\rho^{(n)}$ are series in the activity z of the molecules in the reservoir

$$\rho^{(n)} = \sum_{m=1}^{n} \alpha_{mn} z^m \tag{A.2}$$

Using the matrix techniques described in the text, I have determined $\rho^{(n)}$ for the infinite lattice through $n = 15$. The α_{mn} are listed below, where the value of n is indicated and m increases from one to n across the appropriate row of numbers:

$(n=1)$: 1
$(n=2)$: 1; 3
$(n=3)$: 1; 6; 11
$(n=4)$: 1; 9; 35; 47
$(n=5)$: 1; 12; 76; 216; 227
$(n=6)$: 1; 15; 142; 646; 1413; 1215
$(n=7)$: 1; 18; 249; 1620; 5523; 9778; 7107
$(n=8)$: 1; 21; 429; 3741; 17,595; 47,999; 71,431; 44,959
$(n=9)$: 1; 24; 746; 8316; 50,268; 187,360; 427,814; 549,612; 305,091
$(n=10)$: 1; 27; 1328; 18,188; 134,694; 641,750; 1,998,000; 3,929,620; 4,443,145; 2,206,399
$(n=11)$: 1; 30; 2431; 39,528; 346,394; 2,023,324; 8,056,734; 21,574,840; 37,278,693; 37,645,606; 16,913,987
$(n=12)$: 1; 33; 4567; 85,675; 865,674; 6,029,402; 29,522,654; 101,015,286; 237,229,301; 365,503,237; 333,495,179; 136,823,263

($n=13$): 1; 36; 8760; 185,328; 2,117,145; 17,258,072; 101,269,816; 425,622,128; 1,274,536,419; 2,664,215,044; 3,703,507,408; 3,082,040,416; 1,163,490,499
($n=14$): 1; 39; 17,058; 399,954; 5,088,699; 47,958,961; 331,446,668; 1,666,172,700; 6,111,939,191; 16,256,789,801; 30,611,843,794; 38,763,132,626; 29,651,828,109; 10,366,252,031
($n=15$): 1; 42; 33,557; 860,652; 12,054,453; 130,398,854; 1,048,847,593; 6,187,394,472; 27,047,464,483; 87,908,857,526; 210,267,251,071; 360,192,872,556; 418,797,337,830; 296,407,762,586; 96,491,364,675

APPENDIX B

In this Appendix I evaluate the leading terms in the series in ρ_∞ for ω_0, the limiting relaxation parameter. Equation (8.3) expresses $d\rho/dt$ as a series in ρ (using here ρ, not ρ/ρ_∞ and scaling time to make $c_0=1$)

$$\frac{d\rho}{dt}=\sum_{n=0}^{\infty} c_n\rho^n \tag{B.1}$$

from which a series for ω_0 can be constructed using (8.11),

$$\omega_0=k(s=1)=-\sum_{n=1}^{\infty} nc_n\rho_\infty^n \tag{B.2}$$

The quantities c_n are functions of z (shorthand for z_∞) which in turn is a function of ρ_∞. Thus, in order to extract the total ρ_∞ dependence of ω_0 we need the z dependence of the c_n. The first coefficients are

$$\begin{aligned}
c_0&=1\\
c_1&=-(3+1/z)\\
c_2&=2/2!\\
c_3&=4/3!\\
c_4&=[16+4(1/z)]/4!\\
c_5&=[96+72(1/z)+8(1/z)^2]/5!\\
c_6&=[768+1152(1/z)+320(1/z)^2+24(1/z)^3]/6!
\end{aligned} \tag{B.3}$$

From (5.7) the relation between ρ and z is

$$\frac{\rho}{z}=\frac{1-2\rho}{1-\rho}=1-3\rho+\rho^2+\rho^3+\rho^4+\cdots \tag{B.4}$$

We cannot calculate the coefficients of ρ_∞^m exactly, because there are contributions to the coefficients from all the c_n beyond a certain n. For example, the coefficients c_3, c_4, c_5,... all contribute to the coefficient of ρ_∞^3. For the case of ρ_∞^3 one sees from (B.3) that the contributions will be respectively [I give a few more terms than are shown in (B.3)]

$$4/3!,\quad 4/4!,\quad 8/5!,\quad 24/6!,\quad 96/7!,\quad 480/8!,... \tag{B.5}$$

which is easily generalized to $4(n-3)!/n!$, giving as the net contribution to the coefficient of ρ_∞^3

$$4\sum_{n=3}^{\infty}\frac{n(n-3)!}{n!}=4\sum_{n=3}^{\infty}\frac{1}{(n-1)(n-2)}=4\sum_{m=1}^{\infty}\frac{1}{m(m+1)}=4 \tag{B.6}$$

In this manner we can obtain the beginning terms in the series expansion of ω_0 in powers of ρ_∞:

$$\text{(exchange only)} \qquad \omega_0=1-\rho_\infty^2-3\rho_\infty^3+\cdots \tag{B.7}$$

Using (5.11) with the scaling relation of (7.4), one obtains for the limit of internal equilibration

$$\text{(internal equilibration)} \qquad \omega_0=1-\rho_\infty^2-2\rho_\infty^3+\cdots \tag{B.8}$$

Thus, one sees that the two functions only slowly diverge from one another.

APPENDIX C

In this Appendix I show how the time series for finite ξ and infinite ξ (the limit of internal equilibration) are related. The parameter ξ is the rate constant for internal diffusion, as shown in (9.1). Note that the $\rho^{(n)}$ as given by (9.2) has the form

$$\rho^{(n)}=\sum_{k=1}^{3}a_{kn}z^k+\sum_{k=4}^{n}z^k\sum_{j=0}^{m-4}a_{jkn}\xi^j \qquad (n>3) \tag{C.1}$$

Constructing $\rho(t)$ for finite ξ

$$\rho(t)=\sum_n \rho^{(n)}t^n/n! \tag{C.2}$$

one then forms the $\rho^{(n)}$ in the limit that $\xi\to\infty$ by taking the double limit

$$(\lim t\to 0,\ \xi\to\infty) \qquad d^i\{\rho^{(n)}t^n/n!\}/dt^i \tag{C.3}$$

such that

$$(\lim t \to 0, \xi \to \infty) \qquad \xi t \to 1 \tag{C.4}$$

With (C.3) and (C.4) one finds that a_{jkn} contributes to the z^k coefficient of $\rho^{(n-j)}$. Then in the limit $\xi \to \infty$

$$\rho^{(n)} = \sum_{k=1}^{3} a_{kn} z^k + \sum_{k=4}^{n} a'_{kn} z^k \qquad (n > 3) \tag{C.5}$$

where

$$a'_{kn} = \sum_{L=n}^{\infty} a_{L-n,k,n}/(L-n)! \tag{C.6}$$

and one has the result that $\rho^{(n)}$ for $\xi = \infty$ has contributions from all the $\rho^{(i)}$ for finite ξ with $i > n$. Of course, we know the $\rho^{(n)}$ for $\xi = \infty$ exactly from knowledge of the limit of internal equilibration.

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