

## **Relaxation in Cooperative Systems: Use of Mixture Virial Coefficients**

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The coefficients in power series in the variable time that describe relaxation in a cooperative system can be calculated using a combinatorial approach where one considers how many ways one can introduce a given number of properly defined events in a system. The coefficients obtained in this manner can be related to the equilibrium virial coefficients for a mixture. If one assumes rapid internal equilibration, the relaxation process can be expressed completely in terms of the virial coefficients for a mixture with at most one solute particle, or, in some cases, just the virial coefficients for a single-component system. Thus, equilibrium virial coefficients can give useful information about the time evolution of processes in cooperative systems.

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**KEY WORDS:** Cooperative relaxation; time power series; virial series; kinetic Ising model.

### **1. INTRODUCTION**

Recently<sup>(1,2)</sup> extensive exact power series in the time have been obtained for the cooperative binding of particles to a one-dimensional lattice using matrix techniques to determine the coefficients in the series. In the present work we consider the general question of the relation of the coefficients in a time power series to the coefficients in equilibrium activity (Mayer) series. We begin with a general description of the series. We will use the language of cooperative adsorption of particles to a lattice surface as a specific example; the general approach applies to any cooperative system, not just discrete space lattice models.

Let  $\mathbf{p}$  be a row vector the components of which represent the probabilities of various particle configurations. We consider time processes that

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can be described by the first-order interconversion of the various particle configurations, that is, the dynamics is described by

$$d\mathbf{p}/dt = -\mathbf{p}\mathbf{W} \quad (1.1)$$

where  $\mathbf{W}$  is the appropriate matrix of rate constants. The  $n$ th derivative of  $\mathbf{p}$  evaluated at  $t=0$  is

$$d^n \mathbf{p}/dt^n = (-1)^n \mathbf{p}(0)\mathbf{W}^n \quad (1.2)$$

Let  $\mathbf{v}^+$  be a column vector whose general element is the number of particles in the  $n$ th lattice configuration. Then one has the general relation for the average density

$$\rho(t) = \mathbf{p}(t) \cdot \mathbf{v}^+ / N \quad (1.3)$$

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

$$\rho(t) = \sum_{n=0}^{\infty} \rho^{(n)} t^n / n! \quad (1.4)$$

and using (1.2) and (1.3), one has

$$\rho^{(n)} = N^{-1} (-1)^n \mathbf{p}(0)\mathbf{W}^n \mathbf{v}^+ \quad (1.5)$$

This is the approach<sup>(1,2)</sup> that we have used previously to obtain the coefficients  $\rho^{(n)}$  for cooperative adsorption to a one-dimensional lattice.

Now  $\rho^{(n)}$  in (1.5) has the form of a sum over products of rate constants; if  $k$  is a general rate constant, then  $\rho^{(n)}$  is a sum over terms of the type  $k^n$  (through the  $\mathbf{W}^n$  term). Specifically, with  $\{\sigma\}$  representing a particular sequence of rate constants,

$$\rho^{(n)} = \sum_{\{\sigma\}} \text{sgn}\{\sigma\} \omega\{\sigma\} \prod_{i=1}^n k_i\{\sigma\} \quad (1.6)$$

where  $\text{sgn}\{\sigma\}$  is  $\pm 1$ , depending on  $\{\sigma\}$ , and  $\omega\{\sigma\}$  is a weight factor arising from the occupation numbers in the vector  $\mathbf{v}^+$  and any degeneracy factors in  $\mathbf{W}$ .

Thus, one can think of  $\rho^{(n)}$  as representing a sum over all ways to place  $n$  events on the lattice (an event being represented by a rate parameter). Thus, our approach is to calculate the coefficients  $\rho^{(n)}$  in the same manner that one calculates virial coefficients for equilibrium problems. In particular, if one is given the grand partition function for a lattice gas

$$\Xi = \sum Q(n, N) z^n \quad (1.7)$$

where  $z$  is the activity and  $Q(n, N)$  is the canonical partition function for placing  $n$  particles on a lattice of  $N$  sites, the density is given by

$$\rho = \frac{1}{N} \frac{\partial \ln \Xi}{\partial \ln z} \quad (1.8)$$

or

$$\rho = \sum_n n b_n z^n \quad (1.9)$$

where the  $b_n$  are the coefficients in the Mayer activity series for the pressure

$$p/kT = \sum_n b_n z^n \quad (1.10)$$

which can be converted to the standard virial series for the pressure, or vice versa,

$$p/kT = \sum_n B_n \rho^n \quad (1.11)$$

Now in general<sup>(3)</sup>  $Q(n, N)$  can be written as a power series in  $N$ ,

$$Q(n, N) = Nq_1(n) + \dots \quad (1.12)$$

The  $b_n$  turn out<sup>(3)</sup> to be simply the part of  $Q(n, N)$  linear in  $N$ , i.e.,

$$b_n = q_1 \quad (1.13)$$

We will show that there is a similar construction possible for  $\rho(t)$ , that is, the  $\rho^{(n)}$  of (1.5) can be written as the linear part of the appropriate partition function-like quantity.

In the next section we will illustrate the combinatorial approach to the calculation of the coefficients  $\rho^{(n)}$  in (1.6), that is, we will enumerate the number of ways of arranging  $n$  events. This will then be followed by a more general treatment of the combinatorics in terms of partition function-like quantities.

## 2. COMBINATORICS OF KINETICS

### 2.1. Irreversible Binding in Hard-Particle Systems

In Eq. (1.5) we showed that  $\rho^{(n)}$  involves the sum of terms of the form  $k^n$ , that is, products of rate constants for  $n$  events. We must now be more

precise about what an event is. To be concrete, we take the simplest example, the reaction



which has the rate equations

$$dA/dt = -kA \quad A(t=0) = 1 \quad (2.2)$$

$$dB/dt = kA \quad B(t=0) = 0 \quad (2.3)$$

Equations (2.2)–(2.3) have the simple solutions

$$A(t) = e^{-kt} = 1 - kt + (kt)^2/2! - \dots \quad (2.4)$$

$$B(t) = 1 - e^{-kt} = kt - (kt)^2/2! + \dots \quad (2.5)$$

As a concrete model, we will interpret (2.1) as the irreversible addition of a particle to a vacant site (i.e., an adsorption model where the particle comes from a reservoir at constant activity). Thus we write



where now  $A$  is “0” and  $B$  is “1”; loss of  $A$  represents the binding of a particle at an empty site, while  $B$  is simply the probability that the site is occupied.

In a small interval of time  $\Delta t$ ,  $A$  and  $B$  change as follows:

$$A(t + \Delta t) = A(t) - k \Delta t \quad (2.7)$$

$$B(t + \Delta t) = B(t) + k \Delta t \quad (2.8)$$

From (2.7), (2.8) we can identify two processes:  $A$  either remains the same with probability  $A(t) - k \Delta t$ , or  $A$  changes to  $B$ , the addition of a particle from a reservoir in our model, with probability  $k \Delta t$ . We will refer to the process whereby  $A$  remains unchanged as a pause. Our two events are thus

$$\text{Event I: add a particle} \quad (2.9)$$

$$\text{Event II: pause}$$

Referring to (2.7), (2.8), we see that we can associate the following kinetic parameters with the appropriate events:

$$\begin{aligned} \text{(I) addition of a particle: } &+k \\ \text{(II) pause: } &-k \end{aligned} \quad (2.10)$$

Thus, one can have  $n$  events which can vary in kind from being all particles added, all pauses, or any mixture of the two. Thus, we are led to the combinatorial question of how many ways one can arrange the addition of  $m$  particles and  $(n - m)$  pauses onto the lattice and to the consideration of the analog of the Mayer coefficients for a two-component mixture, the two components being the two kinds of events in (2.9). We will use this idea to rederive the series in (2.4), (2.5). Of course, the ultimate point is that the same procedure can be used when there is interaction between the particles (and pauses!) and hence can be used to treat cooperative relaxation.

We will use the above ideas to treat a lattice of  $N$  sites. We introduce the generating function for  $n$  events

$$\Phi_n = \sum_{m=0}^n k^m (-k)^{n-m} \zeta^m \sum_{\{m,n\}} \Omega\{m,n\} \tag{2.11}$$

where  $\{m, n\}$  indicates a specific sequence of  $n$  events containing the addition of  $m$  particles and  $(n - m)$  pauses;  $Q\{m, n\}$  is a combinatorial factor that gives the number of ways one can arrange  $m$  particles and  $(n - m)$  pauses. Each particle contributes a factor  $k$ , while each pause contributes a factor  $(-k)$ . The quantity  $\zeta$  is an activitylike parameter that simply counts the number of particles. Writing the average number of sites occupied at time  $t$  as a series

$$\langle M(t) \rangle = \sum_{n=0}^{\infty} A_n t^n / n! \tag{2.12}$$

then from our previous discussion we make the identification

$$A_n = \left( \frac{\partial \Phi}{\partial \zeta} \right)_{\zeta=1} = k^n \sum_{m=0}^n m (-1)^{n-m} \sum_{\{m,n\}} Q\{m,n\} \tag{2.13}$$

The average density per site is then

$$\rho(t) = N^{-1} \langle M(t) \rangle \tag{2.14}$$

As mentioned earlier, one finds that the  $Q$  are in general finite polynomials in  $N$ , i.e.,

$$Q\{m,n\} = \sum_{j=1}^n q_j\{m,n\} N^j \tag{2.15}$$

Since  $\rho(t)$  is an intensive quantity, it must be that the contributions of the  $N^j$  terms for  $j > 1$  in (2.15) cancel in (2.13). Defining the analog of a Mayer coefficient

$$b\{m,n\} = q_1\{m,n\} \tag{2.15a}$$

one has

$$\rho^{(n)} = k^n \sum_{m=0}^n m(-1)^{n-m} \sum_{\{m,n\}} b\{m,n\} \tag{2.16}$$

To illustrate the use of (2.16), we will treat a lattice of  $N$  sites where each site can undergo the reaction  $0 \rightarrow 1$  as illustrated in (2.6) independent of the state of occupation of any of the other sites. [The solution is, of course,  $\rho(t) = B(t)$ , with  $B(t)$  given in (2.5).] First we will treat a single site, i.e.,  $N = 1$ . The possible events are outlined in Fig. 1. Since there is only one site, one has (recall that  $\{m, n\}$  indicates  $n$  events,  $m$  of which are the addition of particles)

$$\begin{aligned} b\{m,n\} &= 0 && \text{for } m > 1 \\ b\{1,n\} &= (1)^n = 1 && \text{for } m = 1 \end{aligned} \tag{2.17}$$

Using (2.17) in (2.16) gives the result of (2.5) for  $B(t) = \rho(t)$ .

Now we take a lattice of  $N$  sites and we derive the same result. We will use a linear lattice, since that is easier to draw; since the sites are independent, the geometry of the lattice is immaterial. The possible events through  $n = 2$  are shown in Fig. 2, where the  $Q\{m, n\}$  are indicated explicitly. The

Event Number:

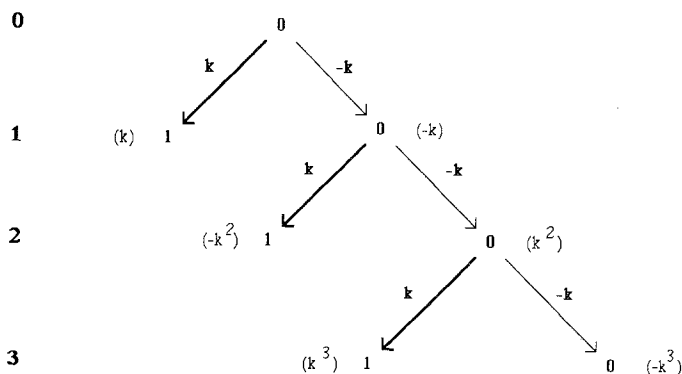


Fig. 1. Illustration of the possible sequence of events for a single site with the irreversible reaction  $0 \rightarrow 1$ . The addition of a particle is shown by the heavy arrows with the rate parameter  $k$ ; pauses (the state remaining 0) are indicated with thin arrows and rate parameter  $-k$ . The net product of rate constants leading to a particular state is shown in parentheses next to the appropriate species.

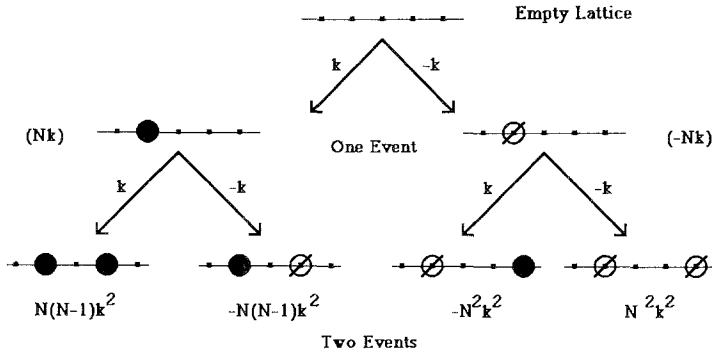


Fig. 2. Illustration of the possible sequences of events for a one-dimensional lattice of  $N$  sites where each site can undergo the reaction  $0 \rightarrow 1$  independent of the state of its neighbors. A solid circle indicates a particle, while an open circle indicates a pause. The combinatorial factors, indicating how many similar configurations there are, are shown, as is the appropriate product of rate constants.

$Q\{m, n\}$  shown are [where we use  $\{\dots\}$  to indicate the actual sequence of particles (1's) and pauses ( $\phi$ 's)]

$$\begin{aligned}
 Q\{\phi\} &= N, & Q\{1\} &= N \\
 b\{\phi\} &= 1, & b\{1\} &= 1 \\
 Q\{\phi\phi\} &= N^2, & Q\{1\phi\} &= N(N-1), \\
 Q\{\phi 1\} &= N^2, & Q\{11\} &= N(N-1) \\
 b\{\phi\phi\} &= 0, & b\{1\phi\} &= -1, \\
 b\{\phi 1\} &= 0, & b\{11\} &= -1
 \end{aligned}
 \tag{2.18}$$

Then, using (2.18) in (2.16), one again has the expansion of (2.5) for  $B(t) = \rho(t)$ :

$$\begin{aligned}
 \rho^{(1)} &= kb\{1\} = k \\
 \rho^{(2)} &= k^2(-b\{1\phi\} + 2b\{11\}) = -k^2
 \end{aligned}
 \tag{2.19}$$

The combinatorics given in Fig. 2 illustrate the fact that  $Q\{m, n\}$  depends on the order in which the events take place. A particle or a pause never can be placed on a lattice site already occupied by a previous particle, but a particle or a pause can be placed on a site already occupied by a pause (because a pause is not a real particle—but the pause combinatorics make a real contribution to the final result).

Of course the point of giving the lattice-combinatorial derivation of

the series for the simple process of (2.6) is that this method can be easily used to treat cases where the particles do interact. As a simple modification of the model illustrated in Fig. 2, take the case where a particle cannot be added to a site if the nearest-neighbor site is already occupied (one-dimensional lattice gas with nearest-neighbor exclusion). Figure 3 shows the analog of Fig. 2, that is, all events through  $n=2$ , except now the combinatorial factors are altered to take into account the fact that one has nearest-neighbor exclusion. The changes from the combinatorial factors given in (2.18) are

$$\begin{aligned} Q\{1\phi\} &= N(N-3) + N^2, & b\{1\phi\} &= -3 \\ Q\{11\} &= N(N-3), & b\{11\} &= -3 \end{aligned} \tag{2.20}$$

the difference being that instead of the  $N(N-1)$  factor, one has  $N(N-3)$ . For independent particles there are  $N$  ways to place the first particles and  $(N-1)$  ways to place the second one, while with nearest-neighbor exclusion there are  $(N-3)$  ways to place the second particle. Using (2.20) in (2.19), one has

$$\rho^{(1)} = k, \quad \rho^{(2)} = -3k^2 \tag{2.21}$$

In a similar fashion, one can calculate higher-order terms using the appropriate combinatorial factors  $Q\{m, n\}$  (or their linear parts, the  $b\{m, n\}$ ).

We can simplify (2.16) considerably. To that end, we introduce the following notation. In general  $\{m, n\}$  means a sequence of  $n$  events,  $m$  of which are the addition of particles. If we want to specify some of the specific events, we will write, for example,  $\{1; m, n-2; \phi\}$ , which indicates that the first event is the addition of a particle and the last event is a pause,

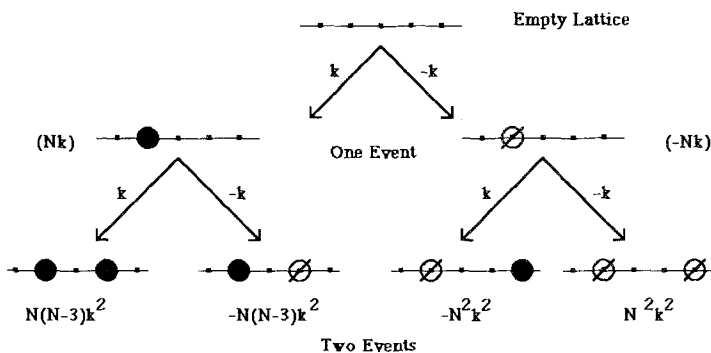


Fig. 3. Illustration of the possible sequences of events for a one-dimensional lattice of  $N$  sites where each site can undergo the irreversible reaction  $0 \rightarrow 1$ . This is the same picture as in Fig. 2, except that here there is nearest-neighbor exclusion, which alters the combinatorial factors and hence the coefficients  $\rho^{(n)}$ .



the two separated by  $(n-2)$  events,  $m$  of which are the addition of particles. As another example, the sequence  $\{\phi: m, n-1\}$  indicates that the first event is a pause followed by  $(n-1)$  events,  $m$  of which are the addition of particles. If we want to specify all of the events, we will write  $\{1\phi1\phi\}$ , etc.

Using the above notation, we notice that all sequences that begin with a pause,  $\{\phi: m, n-1\}$ , do not contribute to  $\rho^{(n)}$  for the initial condition of an empty lattice. This is so because there are  $N$  ways to place the initial  $\phi$  and then  $N$  times that number of ways of placing whatever event follows (particle or pause). Thus, the combinatorial term has a factor  $N^2$  and cannot contain a term linear in  $N$ ; hence, it does not contribute to  $\rho^{(n)}$ . In addition, all configurations of the form  $\{m, n-1; \phi\}$  can be ignored. This is so because

$$b\{m, n-1; \phi\} = b\{m, n-1; 1\}$$

i.e., with respect to the final event, the combinatorics are identical whether the event is a particle or a pause. The contributions of the above configurations to (2.16) are given by

$$\begin{aligned} k^n[(m+1)(-1)^{n-(m+1)} b\{m, n-1; 1\} + m(-1)^{n-m} b\{m, n-1; \phi\}] \\ = k^n(-1)^{n-(m+1)} b\{m, n-1; 1\} \end{aligned} \tag{2.22}$$

Note that the two terms combine to give the contribution of just the  $b\{m, n-1; 1\}$  term, except that the  $(m+1)$  factor is missing. The result of (2.22) and the observation made previously that sequences starting with a pause do not contribute means that we need consider only sequences of events of the form  $\{1; m, n-2; 1\}$  and in so doing modify (2.16) to suppress the factor  $m$  [because it cancels in (2.22)]. Thus, for the initial conditions of an empty lattice we have the results

$$\begin{aligned} \rho^{(1)} &= kb\{1\} \\ \rho^{(n)} &= k^n \sum_{m=0}^{n-2} (-1)^{n-2-m} b\{1; m, n-2; 1\} \quad (n \geq 2) \end{aligned} \tag{2.23}$$

Equations (2.23) through  $n=4$  read

$$\begin{aligned} \rho^{(0)} &= 0 \\ \rho^{(1)} &= kb\{1\} \\ \rho^{(2)} &= k^2 b\{11\} \\ \rho^{(3)} &= k^3 (b\{111\} - b\{1\phi1\}) \\ \rho^{(4)} &= k^4 (b\{1111\} - b\{11\phi1\} - b\{1\phi11\} + b\{1\phi\phi1\}) \end{aligned} \tag{2.24}$$

We now show that most of the  $b\{m, n\}$  appearing in (2.24) can be related to the equilibrium  $b_n$ . We first note that  $(\{n, n\})$  indicates  $n$  events all of which are the addition of particles)

$$b\{n, n\} = b_n^* = n! b_n \quad (2.25)$$

This result follows since  $b\{n, n\}$  represents the successive addition of  $n$  particles. The combinatorics of the number of ways of arranging  $n$  such events on the lattice is the same as for the equilibrium case, except that in the time problem the events (addition of particles) are distinguishable because they occur in a specific sequence in time (in the equilibrium case one divides by  $n!$ , since the particles are identical). The second relation one has is as follows (where  $\phi^i$  represents  $i$  consecutive  $\phi$ 's and  $1^j$  represents  $j$  consecutive 1's)

$$b\{1\phi^i 1^j\} = (b_2^*)^i b_{j+1}^* \quad (2.26)$$

This result follows because the  $i$  consecutive pauses are equivalent to adding a second particle  $i$  times; with respect to the  $1^j$  sequence of events, the  $\phi^i$  do not effect the combinatorics, and hence one has  $b_{j+1}^*$ .

Using (2.25) and (2.26), the equations of (2.24) become (recognizing that  $b_1^* = b_1 = 1$ , since there are  $N$  ways to place the first particle on the lattice)

$$\begin{aligned} \rho^{(0)} &= 0 \\ \rho^{(1)} &= k \\ \rho^{(2)} &= k_2[2b_2] \\ \rho^{(3)} &= k^3[6b_3 - 4b_2^2] \\ \rho^{(4)} &= k^4[24b_4 - 12b_2b_3 + 8b_2^3 - b\{11\phi 1\}] \end{aligned} \quad (2.27)$$

where  $b_2$ ,  $b_3$ , and  $b_4$  are the equilibrium  $b_n$ . The only new quantity is  $b\{11\phi 1\}$ . For higher-order terms, more and more new terms would appear. For example,

$$\begin{aligned} \rho^{(5)} &= k^5[b\{11111\} - b\{111\phi 1\} - b\{11\phi 11\} - b\{1\phi 111\} \\ &\quad + b\{11\phi\phi 1\} + b\{1\phi\phi 11\} + b\{1\phi 1\phi 1\} - b\{1\phi\phi\phi 1\}] \\ \rho^{(5)} &= k^5[120b_5 - 48b_2b_4 + 24b_2^2b_3 - 16b_2^4 + 2b_2b\{11\phi 1\} \\ &\quad - b\{111\phi 1\} - b\{11\phi 11\} + b\{11\phi\phi 1\}] \end{aligned}$$

which requires the special construction of the three new kinetic terms  $b\{111\phi 1\}$ ,  $b\{11\phi 11\}$ , and  $b\{11\phi\phi 1\}$ , in addition to the term  $b\{11\phi 1\}$  already required to construct  $\rho^{(4)}$ .

As an example of the use of (2.27), let us again take the case of independent particles. In that case the equilibrium canonical partition function is

$$Q_n = \frac{N!}{n!(N-n)!} = \frac{N(N-1)(N-2)\cdots(N-n+1)}{n!}$$

and  $b_n$  is the linear part of  $Q_n$  with respect to  $N$ ,

$$b_n = (-1)^{n+1} \left( \frac{1}{n} \right) \quad (2.28)$$

For the special term  $b\{11\phi1\}$  one has the combinatorial factor (notice that one does not divide by  $n!$ , since the events are distinguishable by sequence)

$$Q\{11\phi1\} = N(N-1)(N-2)^2 \quad (2.28a)$$

The desired quantity is the part of  $Q$  linear in  $N$ :

$$b\{11\phi1\} = -4 \quad (2.29)$$

Using (2.28) and (2.29) in (2.27), one has

$$\rho^{(1)} = k, \quad \rho^{(2)} = -k^2, \quad \rho^{(3)} = k^3, \quad \rho^{(4)} = -k^4$$

and one once again has the expansion of (2.4) for  $B(t) = \rho(t)$ .

For the model of Fig. 3, i.e., nearest-neighbor exclusion, we quote the results for the equilibrium  $b_n$  through  $n=4$ :

$$b_1 = 1, \quad b_2 = -1\frac{1}{2}, \quad b_3 = 3\frac{1}{3}, \quad b_4 = -8\frac{3}{4} \quad (2.30)$$

The equilibrium  $b_3$  is obtained from the following combinatorial expression:

$$Q_3 = \frac{1}{3!} [2N(N-5) + N(N-5)(N-6)]$$

This is easily modified to give the combinatorial expression for  $\{11\phi1\}$ , since one simply repeats the final factor in each term and deletes the  $n!$ :

$$Q\{11\phi1\} = [2N(N-5)^2 + N(N-5)(N-6)^2]$$

This gives (taking the part of the above expression linear in  $N$ )

$$b\{11\phi1\} = -130 \quad (2.31)$$

Using (2.30) and (2.31) in (2.27), one has

$$\begin{aligned}
 \rho^{(0)} &= 0 \\
 \rho^{(1)} &= k \\
 \rho^{(2)} &= -3k^2 \\
 \rho^{(3)} &= 11k^3 \\
 \rho^{(4)} &= -47k^4
 \end{aligned}
 \tag{2.32}$$

To illustrate the utility and generality of (2.27), we treat the two-dimensional lattice gas on the square lattice with nearest-neighbor exclusion. The first four equilibrium  $b_n$  are (from Ising series<sup>(4)-(6)</sup>)

$$b_1 = 1, \quad b_2 = -2\frac{1}{2}, \quad b_3 = 10\frac{1}{3}, \quad b_4 = -52\frac{1}{4}$$

In analogy with the calculation of  $b\{11\phi 1\}$  for the one-dimensional lattice with nearest-neighbor exclusion, one has

$$\begin{aligned}
 Q_3 &= \frac{1}{3!} [4N(N-8) + 4N(N-9) + N(N-13)(N-10)] \\
 Q\{11\phi 1\} &= [4N(N-8)^2 + N(N-9)^2 + N(N-13)(N-10)^2], \\
 b\{11\phi 1\} &= -720
 \end{aligned}$$

giving

$$\begin{aligned}
 \rho^{(1)} &= k \\
 \rho^{(2)} &= -5k^2 \\
 \rho^{(3)} &= 37k^3 \\
 \rho^{(4)} &= -349k^4
 \end{aligned}
 \tag{2.33}$$

One can apply (2.27) to irreversible adsorption in any hard-particle system, lattice gases, or particles in continuous space.

## 2.2. Reversible Binding in Hard-Particle Systems

The treatment of reversible binding is simply an extension of the ideas already presented. The basic reaction is the exchange of a particle with a

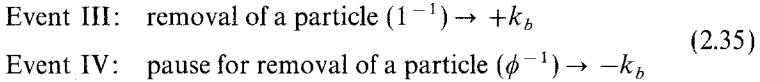
<sup>2</sup> The  $b_n$  for the hard-particle lattice gas are obtained as a byproduct of the series for the Ising model. The first 13  $b_n$  are given in ref. 5. The 14th and 15th terms are found in ref. 6.

reservoir where the state of a lattice site can go reversibly from 0 (vacant) to 1 (occupied):

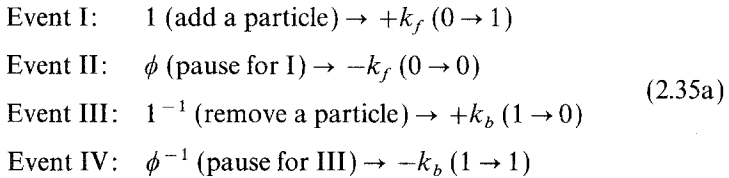


where  $k_f$  and  $k_b$  are the rate constants for the adsorption and desorption, respectively, of a particle. For hard particles, the possibility of the forward step may depend on the state of occupancy of neighboring sites.

One now has two additional types of events:



where we have indicated the symbols we will use to represent these events ( $1^{-1}$  and  $\phi^{-1}$ ); the rate parameter,  $+k_b$  or  $-k_b$ , assigned to each event is also indicated. The total list of events is now [combining (2.35) and (1.9), (2.10), using the rate constant  $k_f$  for the events in (2.10)]:



The symbols used to indicate the various processes are indicated, as are the rate parameters (and the appropriate sign); the processes in parentheses indicate the actual physical change taking place—the pauses do not change the state of the lattice, but they do contribute to  $\rho(n)$ .

We will now interpret the notation  $\{m, n\}$  to indicate  $n$  events with a net of  $m$  particles; the possible events are to be interpreted as any combination of the processes listed in (2.35a). Equation (2.16) then applies to the reversible case with no modification. The only difference is that now there are many more configurations  $\{m, n\}$  that contribute.

As an illustration, Fig. 4 illustrates the different possible combination of events through  $n=2$  for independent particles (the case that was illustrated for irreversible binding in Fig. 2). The combinatorial factors  $Q\{m, n\}$  are shown, as are the appropriate products of rate constants. The parts of the illustrated  $Q\{m, n\}$  linear in  $N$  are shown below, as is the construction of  $\rho^{(1)}$  and  $\rho^{(2)}$ :

$$\begin{aligned} \rho^{(0)} &= 0 \\ \rho^{(1)} &= k_f \\ \rho^{(2)} &= -k_f^2 - k_f k_b \end{aligned} \quad (2.36)$$

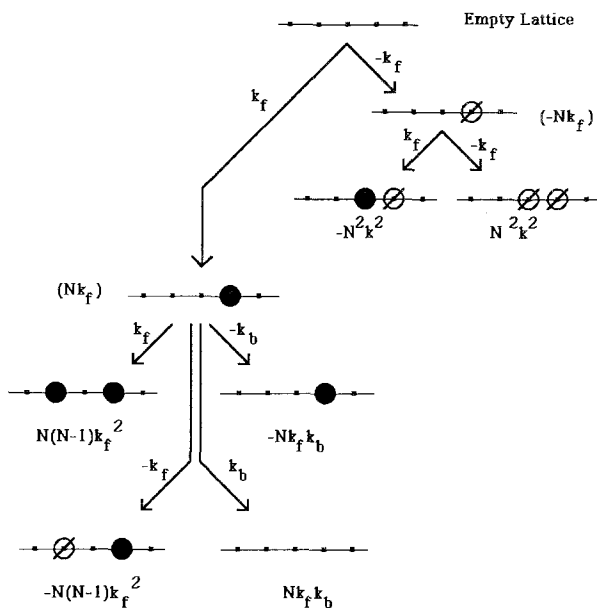


Fig. 4. Illustration of the possible sequences of events for a one-dimensional lattice of  $N$  sites where each site can undergo the reversible reaction  $0 \leftrightarrow 1$  independent of the states of neighboring sites. Particles are indicated by solid circles, while pauses are indicated by open circles. This scheme is the generalization of Fig. 2 to the reversible case.

All of the specific configurations that contribute to  $\rho^{(n)}$  through  $n = 4$  for reversible bonding are shown in Table I. Also indicated is the contribution each  $b\{m, n\}$  would make for the special case of hard particles. In constructing Table I, we are using the relation of (2.22) and an analogous relation for the two new type of events one has in reversible binding:

$$\begin{aligned}
 b\{m, n-1; 1^{-1}\} &= b\{m, n-1; \phi^{-1}\} \\
 k_b[-(m+1)b\{m, n-1; \phi^{-1}\} + (m)b\{m, n-1; 1^{-1}\}] \\
 &= -k_b b\{m, n-1; \phi^{-1}\}
 \end{aligned}
 \tag{2.37}$$

where we have given the rate constants and signs just for the last event (the product of rate constants and sign for the first  $n-1$  events is the same in each case). Also left out of Table I are other configurations whose contribution to the  $\rho^{(n)}$  will cancel, specifically, those configurations where the appropriate  $Q\{m, n\}$  have no linear term in  $N$ , e.g.,  $\{11^{-1}1\}$ ,  $\{1\phi^{-1}1\}$ , and  $\{1\phi^{-1}1^{-1}1\}$ .

Using the results of Table I for the case of hard particles, one has the following general relations (with  $b_1 = 1$ ):

$$\begin{aligned}
 \rho^{(0)} &= 0 \\
 \rho^{(1)} &= k_f \\
 \rho^{(2)} &= k_f^2 [2b_2] - k_f k_b \\
 \rho^{(3)} &= k_f^3 [6b_3 - 4b_2^2] + k_f^2 k_b [-4b_2] + k_f k_b^2 \\
 \rho^{(4)} &= k_f^4 [24b_4 - 12b_2 b_3 + 8b_2^3 - b\{11\phi 1\}] \\
 &\quad + k_f^3 k_b [-24b_3 + 20b_2^2] + k_f^2 k_b^2 [6b_2] - k_f k_b^3
 \end{aligned}
 \tag{2.38}$$

Table I. The Configurations of the Events Listed in (2.35a) for Reversible Binding That Contribute to  $\rho^{(n)a}$

$n$	Configuration	Contribution for hard particles
1	1	$b_1^* k_f$
2	1 1	$b_2^* k_f^2$
	$1 \phi^{-1}$	$-b_1^* k_f k_b$
3	1 1 1	$b_3^* k_f^3$
	$1 1 \phi^{-1}$	$-2b_2^* k_f^2 k_b$
	$1 \phi 1$	$-(b_2^*)^2 k_f^3$
	$1 \phi \phi^{-1}$	$b_2^* k_f^2 k_b$
	$1 \phi^{-1} 1$	$-b_2^* k_f^2 k_b$
	$1 \phi^{-1} \phi^{-1}$	$b_1^* k_f k_b^2$
4	1 1 1 1	$b_4^* k_f^4$
	$1 1 1 \phi^{-1}$	$-3b_3^* k_f^3 k_b$
	$1 1 \phi 1$	$-b\{1 1 \phi 1\}$
	$1 1 \phi \phi^{-1}$	$2b_3^* k_f^3 k_b$
	$1 1 1^{-1} 1$	$2(b_2^*)^2 k_f^3 k_b$
	$1 1 1^{-1} \phi^{-1}$	$-2b_2^* k_f^2 k_b^2$
	$1 1 \phi^{-1} 1$	$-2b_2^* k_f^2 k_b$
	$1 1 \phi^{-1} \phi^{-1}$	$4b_2^* k_f^2 k_b^2$
	$1 \phi 1 1$	$-b_2^* b_3^* k_f^4$
	$1 \phi 1 \phi^{-1}$	$2(b_2^*)^2 k_f^2 k_b$
	$1 \phi \phi 1$	$(b_2^*)^3 k_f^4$
	$1 \phi \phi \phi^{-1}$	$-(b_2^*)^2 k_f^3 k_b$
	$1 \phi \phi^{-1} 1$	$(b_2^*)^2 k_f^2 k_b$
	$1 \phi \phi^{-1} \phi^{-1}$	$-b_2^* k_f^2 k_b^2$
	$1 \phi^{-1} 1 1$	$-b_3^* k_f^3 k_b$
	$1 \phi^{-1} 1 \phi^{-1}$	$2b_2^* k_f^2 k_b^2$
$1 \phi^{-1} \phi 1$	$b_2^* k_f^3 k_b$	
$1 \phi^{-1} \phi \phi^{-1}$	$-b_2^* k_f^2 k_b^2$	
$1 \phi^{-1} \phi^{-1} 1$	$b_2^* k_f^2 k_b^2$	
$1 \phi^{-1} \phi^{-1} \phi^{-1}$	$-b_1^* k_f k_b^3$	

<sup>a</sup> The contribution of each configuration for the special case of hard-particle systems is also given. The  $b_n^*$  are given in (2.25);  $b_n^* = n! b_n$ . For all hard-particle systems one has  $b_1 = 1$ .

Of course, when  $k_b = 0$  (irreversible binding), (2.38) reduces to (2.27) with  $k = k_f$ . One notes that there are no new factors that need to be evaluated than were needed to treat the case of irreversible binding.

For independent particles, the process of (2.34) is described by the simple differential equation

$$\frac{d\rho}{dt} = k_f(1 - \rho) - k_b\rho \quad (2.39)$$

for which

$$\rho^{(n)} = (-1)^{n+1} k_f(k_f + k_b)^{n-1} \quad (2.40)$$

which are the same results that one gets when (2.28) and (2.29) are used in (2.38).

For the case of reversible binding in the one-dimensional lattice gas with nearest-neighbor exclusion, the use of (2.30) and (2.31) in (2.38) gives

$$\begin{aligned} \rho^{(0)} &= 0 \\ \rho^{(1)} &= k_f \\ \rho^{(2)} &= -3k_f^2 - k_f k_b \\ \rho^{(3)} &= 11k_f^3 + 6k_f^2 k_b + k_f k_b^2 \\ \rho^{(4)} &= -47k_f^4 - 35k_f^3 k_b - 9k_f^2 k_b^2 - k_f k_b^3 \end{aligned} \quad (2.41)$$

The series for this reversible binding in this model are known through  $n = 15$ ; the above results agree with those results obtained in a different manner<sup>(1)</sup> (setting  $k_f = z$  and  $k_b = 1$ ).

For the case of the two-dimensional square lattice with nearest-neighbor exclusion, the use of (2.32) and 2.32b) in (2.38) gives

$$\begin{aligned} \rho^{(0)} &= 0 \\ \rho^{(1)} &= k_f \\ \rho^{(2)} &= -5k_f^2 - k_f k_b \\ \rho^{(3)} &= 37k_f^3 + 10k_f^2 k_b + k_f k_b^2 \\ \rho^{(4)} &= -349k_f^4 - 123k_f^3 k_b - 15k_f^2 k_b^2 - k_f k_b^3 \end{aligned} \quad (2.41)$$

### 3. PARTITION FUNCTIONS FOR KINETICS

In this section we show formally how time series for relaxation processes in lattice gases can be calculated using analogs of activity series.



Let  $\Gamma$  be a set of  $N$  consecutively numbered lattice sites. Let  $\Gamma \supset \gamma_n$  be a subset of  $n$  lattice sites with numbers, not necessarily consecutive, in ascending order. Let  $P(\gamma_n)$  be the *a priori* probability of finding  $n$  particles on the lattice with the configuration  $\gamma_n$ . The master equation for the time evolution of the  $P(\gamma_n)$  is then

$$\begin{aligned} \frac{dP(\gamma_n)}{dt} = & \sum_{\gamma_{n-1} \subset \gamma_n} w^+(\gamma_{n-1}, \gamma_n) P(\gamma_{n-1}) \\ & - \sum_{\gamma_{n-1} \subset \gamma_n} w^-(\gamma_n, \gamma_{n-1}) P(\gamma_n) - \sum_{\gamma_{n+1} \supset \gamma_n} w^+(\gamma_n, \gamma_{n+1}) P(\gamma_n) \\ & + \sum_{\gamma_{n+1} \supset \gamma_n} w^-(\gamma_{n+1}, \gamma_n) P(\gamma_{n+1}) \end{aligned} \quad (3.1)$$

where  $w^+(\gamma_{n-1}, \gamma_n)$  is the transition probability for the addition of a particle to configuration  $\gamma_{n-1}$  to yield  $\gamma_n$  and  $w^-(\gamma_n, \gamma_{n-1})$  is the transition probability for subtracting a particle from configuration  $\gamma_n$  to yield  $\gamma_{n-1}$ .

We express the  $P(\gamma_n)$  as time series

$$\begin{aligned} P(\gamma_n) &= \sum_{m=0}^{\infty} P^{(m)}(\gamma_n) t^m / m! \\ P^{(m)}(\gamma_n) &= \left[ \frac{d^m P(\gamma_n)}{dt^m} \right]_{t=0} \end{aligned} \quad (3.2)$$

Taking the  $w$ 's to be independent of time, substitution of the time series (3.2) into (3.1) yields the recursion relation

$$\begin{aligned} P^{(m)}(\gamma_n) = & \sum_{\gamma_{n-1} \subset \gamma_n} w^+(\gamma_{n-1}, \gamma_n) P^{(m-1)}(\gamma_{n-1}) \\ & - \sum_{\gamma_{n-1} \subset \gamma_n} w^-(\gamma_n, \gamma_{n-1}) P^{(m-1)}(\gamma_n) \\ & - \sum_{\gamma_{n+1} \supset \gamma_n} w^+(\gamma_n, \gamma_{n+1}) P^{(m-1)}(\gamma_n) \\ & + \sum_{\gamma_{n+1} \supset \gamma_n} w^-(\gamma_{n+1}, \gamma_n) P^{(m-1)}(\gamma_{n+1}) \end{aligned} \quad (3.3)$$

The probability of finding  $n$  particles on the lattice in any configuration is given by

$$P_n = \sum_{\gamma_n} P(\gamma_n) \quad (3.4)$$

The average density of particles per site is then

$$\rho = \frac{1}{N} \sum_n n P_n \quad (3.5)$$

Writing  $\rho$  as a time series

$$\rho = \sum_{m=0}^{\infty} \rho^{(m)} t^m / m! \quad (3.6)$$

$$\rho^{(m)} = \left[ \frac{d^m \rho}{dt^m} \right]_{t=0}$$

then (3.3)–(3.6) give for the  $\rho^{(m)}$

$$\rho^{(m)} = N^{-1} \sum_n \sum_{\gamma_{n-1}} \sum_{\gamma_n \supset \gamma_{n-1}} [w^+(\gamma_{n-1}, \gamma_n) P^{(m-1)}(\gamma_{n-1}) - w^-(\gamma_n, \gamma_{n-1}) P^{(m-1)}(\gamma_n)] \quad (3.7)$$

To proceed with the evaluation of the  $\rho^{(m)}$  as given by (3.7), we specifically treat lattice gases in contact with a reservoir of particles having activity  $z$ . For simplicity, we consider the case of a sudden jump in the activity of the reservoir at  $t=0$ ,

$$\begin{aligned} z &= z_0 & \text{for } t < 0 \\ z &= z_\infty & \text{for } t \geq 0 \end{aligned} \quad (3.8)$$

Then for the general reaction



detailed balance gives

$$w^+(\gamma_{n-1}, \gamma_n) / w^-(\gamma_n, \gamma_{n-1}) = z_\infty K(\gamma_{n-1}, \gamma_n) \quad (3.10)$$

where  $K$  is the appropriate ratio of equilibrium Boltzmann factors. We choose to define the following activity-independent rate parameters consistent with (3.10):

$$\begin{aligned} w^+(\gamma_{n-1}, \gamma_n) &= z_\infty k^+(\gamma_{n-1}, \gamma_n) \\ w^-(\gamma_n, \gamma_{n-1}) &= k^-(\gamma_n, \gamma_{n-1}) \end{aligned} \quad (3.11)$$

To begin the recursion process, one has at  $t=0$

$$k^-(\gamma_n, \gamma_{n-1}) P^{(0)}(\gamma_n) = z_0 k^+(\gamma_{n-1}, \gamma_n) P^{(0)}(\gamma_{n-1}) \quad (3.12)$$

Using (3.11) in (3.6) yields

$$\rho^{(1)} = N^{-1}(z_\infty - z_0) \sum_n \sum_{\gamma_{n-1}} P^{(0)}(\gamma_{n-1}) \sum_{\gamma_n \ni \gamma_{n-1}} k^+(\gamma_{n-1}, \gamma_n) \quad (3.13)$$

One can then use (3.13) in (3.6) to give  $\rho^{(2)}$ , and so on.

We now show that the problem of evaluating  $\rho^{(1)}$  as given by (3.13) is equivalent to the evaluation of mixture activity series in equilibrium statistical mechanics. For a single-component lattice gas with activity  $z_0$ , the grand partition function is

$$\begin{aligned} \mathcal{E} &= \sum_n Q_n z_0^n \\ Q_n &= \sum_{\gamma_n} q(\gamma_n) \end{aligned} \quad (3.14)$$

where  $q(\gamma_n)$  is the Boltzmann factor for the configuration of  $n$  particles,  $\gamma_n$ . Then

$$P^{(0)}(\gamma_n) = q(\gamma_n) z_0^n / \mathcal{E} \quad (3.15)$$

Using (3.15), we can rewrite (3.13) as

$$\rho^{(1)} = (N\mathcal{E})^{-1} \sum_n (z_\infty - z_0) z_0^{n-1} \sum_{\gamma_{n-1}} q(\gamma_{n-1}) \sum_{\gamma_n \ni \gamma_{n-1}} k^+(\gamma_{n-1}, \gamma_n) \quad (3.16)$$

Now the configurational canonical partition function for a lattice gas mixture containing one solute particle and  $n - 1$  solvent particles is

$$Q_{1,n-1} = \sum_{\gamma_{n-1}} q_{11}(\gamma_{n-1}) \sum_{\gamma_n \ni \gamma_{n-1}} q_{12}(\gamma_{n-1}, \gamma_n) \quad (3.17)$$

where  $q_{11}$  and  $q_{12}$  are the Boltzmann factors for solvent-solvent and solute-solvent interactions, respectively. The sums appearing in (3.16) are exactly the same as those in (3.17) with  $q_{12}$  replaced by  $k^+$ . One can then write (3.16) as

$$\rho^{(1)} = \left( \frac{z_\infty}{z_0} - 1 \right) \sum_{n=1}^{\infty} c_n z_0^n \quad (3.18)$$

where  $c_n$  is the coefficient in the Mayer double activity series for a binary mixture for one solute and  $n - 1$  solvent particles with the solute-solvent Boltzmann factor  $q_{12}(\gamma_{n-1}, \gamma_n)$  replaced by the rate constant  $k^+(\gamma_{n-1}, \gamma_n)$ .

The expressions for the  $\rho^{(m)}$  for  $m > 1$ , although straightforward to obtain, become quite complicated as  $m$  increases. Since these expressions

often can be simplified for specific models, we will not give general expressions for  $\rho^{(2)}$ , etc., but rather, in the following section, show the results through  $\rho^{(2)}$  for lattice gases with nearest-neighbor interactions only.

#### 4. LATTICE GASES WITH NEAREST-NEIGHBOR INTERACTIONS

In this section we quote the results of applying the approach of the preceding section to lattice gases (any dimension, any coordination number) with nearest-neighbor interactions only. We let  $x$  be the nearest-neighbor interparticle Boltzmann factor

$$x = \exp(-\varepsilon/kT) \quad (4.1)$$

where  $\varepsilon$  is the interparticle interaction energy, and we let  $\kappa^n$  be the rate constant for breaking  $n$  nearest-neighbor interactions (bonds); by taking the form  $\kappa^n$  we assume<sup>(2)</sup> that the activation energy for simultaneously breaking  $n$  nearest-neighbor bonds is linear in  $n$ . In terms of the parameters  $x$  and  $\kappa$  one then has

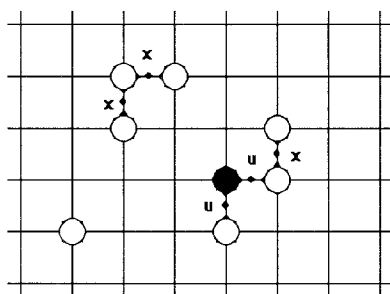
$$\rho^{(0)} = \sum_{n=1}^{\infty} n b_n(x) z_0^n \quad (4.2)$$

$$\rho^{(1)} = \left( \frac{z_{\infty}}{z_0} - 1 \right) \sum_{n=1}^{\infty} c_n(x; x\kappa) z_0^n \quad (4.3)$$

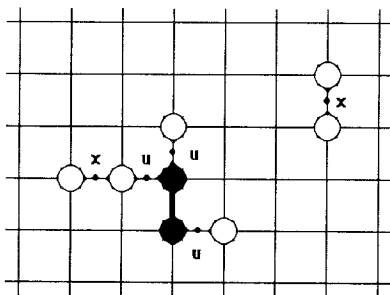
$$\begin{aligned} \rho^{(2)} = & - \left( \frac{z_{\infty}}{z_0} - 1 \right) \left[ z_{\infty} \sum_{n=1}^{\infty} c_n(x; x^2\kappa^2) z_0^n \right. \\ & - (x\kappa - 1) z_{\infty} \sum_{n=1}^{\infty} d_n(x; x\kappa) z_0^n + \sum_{n=1}^{\infty} c_n(x; x\kappa) z_0^n \\ & \left. - x\kappa(1 - \kappa) \sum_{n=1}^{\infty} d_n(x; x\kappa) z_0^{n+1} \right] \quad (4.4) \end{aligned}$$

The quantity  $b_n(x)$  is the standard Mayer coefficient for  $n$  identical particles. As discussed in the previous section,  $c_n(x; u)$  is the Mayer coefficient for a mixture of one solute particle and  $n-1$  solvent particles,  $x$  and  $u$  being respectively, the solvent-solvent and solvent-solute Boltzmann factors. The quantity  $d_n(x; u)$  is the Mayer coefficient for a single dimer solute particle (the dimer occupying any two nearest-neighbor lattice sites) and  $n-1$  solvent particles,  $x$  and  $u$  again being respectively nearest-neighbor solvent-solvent and solute-solvent Boltzmann factors. From the point of view of counting configurations, the dimer is asymmetric

(thus,  $d_1 = 4$  for the plane-square lattice), although both particles in the dimer have the same solvent-solute interaction parameter  $u$  (the dimer is asymmetric because it represents two events that are distinguished by their sequence in time). Figure 5 illustrates sample particle configurations and the assignment of Boltzmann factors involved in the evaluation of the  $b_n$ ,  $c_n$ , and  $d_n$ . The appropriate Mayer coefficients are the part of the appropriate canonical configurational partition function linear in  $N$  (the number of lattice sites). In the Appendix we give some of the  $c_n$  and  $d_n$  for the square planar lattice obtained using the technique of Springgate and Poland<sup>(3)</sup>; the beginning terms for the one-dimensional and three-dimensional cubic lattices are also given.



(a)



(b)

Fig. 5. (a) A sample particle configuration contributing to the coefficient  $c_n$ ; the solid particle represents the solute. The quantities  $x$  and  $u$  are respectively the nearest-neighbor Boltzmann factors for solvent-solvent and solvent-solute interactions. (b) A sample particle configuration contributing to the coefficient  $d_n$ ; the solid particle represents a dimer solute particle. The quantities  $x$  and  $u$  are respectively the nearest-neighbor Boltzmann factors for solvent-solvent and solvent-solute interactions.

Equations (4.2)–(4.4) are the explicit realization for nearest-neighbor lattice gases of the qualitative ideas presented in the introduction:  $\rho^{(1)}$  involves all configurations of one “solute particle” or one event,  $\rho^{(2)}$  involves two events, and so on. In nearest-neighbor lattice gases one has the simplification that the double events that occur in the final formula are nearest-neighbor (resulting in the solute particle being a dimer).

Using the equilibrium relation, (4.2), between  $z$  and  $\rho$ , one can write (4.3) and (4.4) as series in the initial density,

$$\begin{aligned}\rho^{(1)} &= z_\infty \sum_{n=0}^{\infty} \alpha_n^{(+)} \rho_0^n - \sum_{n=1}^{\infty} \alpha_n^{(-)} \rho_0^n \\ \rho^{(2)} &= -\rho^{(1)} \left[ z_\infty \sum_{n=0}^{\infty} \beta_n^{(+)} \rho_0^n + \sum_{n=0}^{\infty} \beta_n^{(-)} \rho_0^n \right]\end{aligned}\tag{4.5}$$

The coefficients in these series are given in the Appendix for the Ising model on the plane-square lattice for the general case of nearest-neighbor attractive interactions and the special case of nearest-neighbor exclusion.

## 5. LIMIT OF INTERNAL EQUILIBRATION

Equation (3.18) gives a general relation for the initial rate of change of density in a cooperative system subject to the initial perturbation described by (3.8):

$$\left(\frac{d\rho}{dt}\right)_{t=0} = \left(\frac{z_\infty}{z_0} - 1\right) \sum_{n=1}^{\infty} c_n z_0^n\tag{5.1}$$

Equation (5.1) applies to both discrete (lattice) and continuous space models, although we have given in detail the derivation only for lattice models. The relation between  $\rho_0$  and  $z_0$  given in (1.9) can be inverted to give  $z_0$  as a function of  $\rho_0$ ,

$$z_0 = \sum_n a_n \rho_0^n\tag{5.2}$$

Using (5.2) in (5.1) gives

$$\left(\frac{d\rho}{dt}\right)_{t=0} = \sum_{n=0}^{\infty} \zeta_n \rho_0^n\tag{5.3}$$

Equation (5.3) gives the initial rate of change of the density in terms of the initial equilibrium density. If as the density varies with time, the intermediate particle configurations have the same probability as for a system

at equilibrium at the same density, then (5.3) will be a general differential equation for the rate of change of the density, i.e.,

$$\frac{d\rho(t)}{dt} = \sum_{n=0}^{\infty} \zeta_n \rho(t)^n \quad (5.4)$$

Equation (5.4) will hold if the rate of internal diffusion is large compared with the rate of exchange of particles with the reservoir, that is, the limit of internal equilibration. In this limit the density dependence of  $d\rho/dt$  is given solely in terms of the quantities  $b_n$  and  $c_n$  [used to calculate the  $\zeta_n$  of (5.4)], which are obtained using the techniques of equilibrium statistical mechanics.

## 6. SPECIAL CASES

From detailed balance and the definitions (3.10) and (3.11) one has the relation

$$k^+(\gamma_{n-1}, \gamma_n)/k^-(\gamma_n, \gamma_{n-1}) = K(\gamma_{n-1}, \gamma_n) \quad (6.1)$$

which gives the condition that the system will evolve with time to the correct final equilibrium state. Equation (6.1) can be used to eliminate  $k^-$  in favor of  $k^+$  and  $K$ . This still leaves the choice of  $k^-$  arbitrary if the only condition imposed is that the system relax to the correct final equilibrium state. For special choices of  $k^+$  the task of obtaining a series for  $\rho(t)$  simplifies greatly.

The first special case is the choice

$$\begin{aligned} k^+ &= K \\ k^- &= 1 \end{aligned} \quad (6.2)$$

The condition  $k^- = 1$  implies that the activation energy for breaking bonds to remove particles is zero. This obviously is an unrealistic limit for particles with attractive interactions, but it is the limit of interest for hard particles, where the only cooperative effect is that of excluded volume. If the relations of (6.2) hold, then  $k^+$  is simply the equilibrium Boltzmann factor between particles at equilibrium. Since the quantity  $c_n$  is the Mayer coefficient for a mixture of one solute and  $n - 1$  solvent particles, when the solute-solvent interaction is the same as the solvent-solvent interaction, the solute becomes a solvent particle with a label. Thus,  $c_n$  can be obtained from the Mayer coefficient for  $n$  solvent particles, the fact that one particle

is labeled being introduced by a factor  $n$  (the number of ways to pick the labeled particle from  $n$  particles). One has then

$$c_n = nb_n \quad (6.3)$$

and

$$\sum_{n=1}^{\infty} c_n z_0^n = \sum_{n=1}^{\infty} nb_n z_0^n = \rho_0 \quad (6.4)$$

For this special case, Eq. (5.4) for  $d\rho/dt$  in the limit of internal equilibration becomes simply

$$\frac{d\rho}{dt} = \left( \frac{z_\infty}{z} - 1 \right) \rho \quad (6.5)$$

The factor  $z$  in (6.5) can be converted to a function of  $\rho$  using (1.9) and (5.2). Note that in this case the time dependence of  $\rho$  can be obtained using only the  $b_n$  from equilibrium statistical mechanics. Equation (6.5) applies both to lattice and continuous space models. Equation (6.5) is easily modified to treat the case of irreversible binding with internal equilibration (that is, once bound, the particles do not leave the lattice, but they do move rapidly about on the surface). In that case one has

$$\frac{d\rho}{dt} = \frac{z_\infty}{z} \rho \quad (6.5a)$$

For the initial condition  $\rho^{(0)} = 0$ , we have seen in (2.38) that the  $\rho^{(n)}$  through  $n = 3$  are given solely in terms of the equilibrium  $b_n$ , even when the rate of internal diffusion is zero. Equation (6.5) gives the same results as (2.38) through  $\rho^{(3)}$  (the reasons for this are explored in more detail elsewhere<sup>(1)</sup>). Beginning with the  $\rho^{(4)}$  term, there begin to be differences in the coefficients  $\rho^{(n)}$  between the limit of internal equilibration, (6.5), and the limit of no internal diffusion, (2.38). Taking  $k_f = z_\infty$  and  $k_b = 1$ , the coefficient  $\rho^{(4)}$  from (6.5) is in general for hard particles

$$\begin{aligned} \rho^{(4)} = & k_f^4(24b_4 - 60b_2b_3 + 40b_3^2) + k_f^3k_b(20b_2^2 - 24b_3) \\ & + k_f^2k_b^2(6b_2) - k_fk_b^3 \end{aligned} \quad (6.6)$$

The case of irreversible binding with internal equilibration is given by setting  $k_0 = 0$  in (6.6). For the one-dimensional and two-dimensional lattice gases with nearest-neighbor exclusion treated in (2.41) and (2.42), respec-



tively, in the limit of zero internal diffusion, we have the comparisons (only the  $\rho^{(4)}$  terms differ), taking  $k_f = k$  and  $k_b = 1$ , for one dimension,

$$\begin{aligned}\rho^{(4)} &= -47k^4 - 35k^3 - 9k^2 - k && \text{(no internal diffusion)} \\ \rho^{(4)} &= -45k^4 - 35k^3 - 9k^2 - k && \text{(internal equilibration)}\end{aligned}\quad (6.7a)$$

and for two dimensions,

$$\begin{aligned}\rho^{(4)} &= -349k^4 - 123k^3 - 15k^2 - k && \text{(no internal diffusion)} \\ \rho^{(4)} &= -329k^4 - 123k^3 - 15k^2 - k && \text{(internal equilibration)}\end{aligned}\quad (6.7b)$$

One sees that the differences in the two limits are very minor; thus, it is not surprising that the limit of internal equilibration serves as a very good approximation to the case of no internal diffusion (except for the very last stages of the relaxation process<sup>(1)</sup>).

The second special case is

$$\begin{aligned}k^+ &= 1 \\ k^- &= K^{-1}\end{aligned}\quad (6.8)$$

In this case the activation energy for adding a particle is zero, while the activation energy for breaking a bond is the negative of the interparticle interaction energy. Since  $k^+ = 1$ , the canonical configurational partition for adding a single solute particle with  $k^+ = 1$  to  $n - 1$  solvent particles is simply  $Q_{1,n-1} = [N - (n - 1)] Q_{n-1}$  if there is no excluded-volume effect beyond a single lattice site [with  $k^+ = 1$ , the solute particle is a noninteracting particle which can be placed anywhere on the  $N - (n - 1)$  remaining sites with the same, zero, energy]. Thus,

$$c_n = -(n - 1)b_{n-1} \quad (6.9)$$

(where  $c_1 = 1$ ) and

$$\sum_{n=1}^{\infty} c_n z_0^n = z_0 - z_0 \sum_{n=1}^{\infty} n b_n z_0^n = z_0(1 - \rho_0) \quad (6.10)$$

With (6.10) one has

$$\frac{d\rho}{dt} = (z_{\infty} - z)(1 - \rho) \quad (6.11)$$

in the limit of internal equilibration. Again, (1.9) and (5.2) can be used to replace  $z$  by  $\rho$  in (6.11), requiring knowledge of the  $b_n$  only.

We note that for a lattice gas of independent particles (the only restriction being that only one particle can occupy a given lattice site) one has  $z = \rho/(1 - \rho)$  and (6.5) and (6.11) both reduce to

$$\frac{d\rho}{dt} = z_{\infty}(1 - \rho) - \rho \quad (6.12)$$

## 7. PROPERTIES OF THE LIMIT OF INTERNAL EQUILIBRATION

Equation (5.4) gives an expression for  $d\rho/dt$  in terms of a series in  $\rho(t)$ , the expansion coefficients  $\zeta_n$  being obtained from the quantities  $b_n$  and  $c_n$  in the limit of internal equilibration. In this section we explore some of the properties of this limit. Kawasaki,<sup>(7)</sup> using Glauber's reduced master equation<sup>(8)</sup> (used to give an exact solution for relaxation in the one-dimensional Ising model for a special choice of transition probabilities<sup>(2)</sup>), has treated spin diffusion in the Ising model near the critical point assuming instantaneous local equilibrium. He showed that under these conditions the diffusion constant goes to zero at the critical point as the inverse of the static magnetic susceptibility and that this was an upper bound for the case when one does not have instantaneous local equilibrium. We will use the virial series approach developed here to give the analogous results for lattice gases.

Writing (5.4) as an activity series, one has<sup>3</sup>

$$\frac{d\rho}{dt} = (z_{\infty} - z) \sum_n c_n z^{n-1} \quad (7.1)$$

Defining the following deviations from the final equilibrium state

$$\begin{aligned} \Delta\rho &= \rho_{\infty} - \rho \\ \Delta z &= z_{\infty} - z \end{aligned} \quad (7.2)$$

then if the final state is not a singular point (i.e., if the final density is not the density of a phase transition), one can expand all functions of  $z$  as a series in  $\Delta\rho$ ,

$$\begin{aligned} \Delta z &= a \Delta\rho + b(\Delta\rho)^2 + \dots \\ \sum_n c_n z^{n-1} &= A + B \Delta\rho + \dots \end{aligned} \quad (7.3)$$

<sup>3</sup> The coefficients  $c_n$  contain both equilibrium Boltzmann factors and rate constants. For a similar approach to the treatment of the kinetics of conformational transitions in biopolymers see ref. 9.

where

$$a = \left( \frac{\partial z}{\partial \rho} \right)_{z=z_\infty} \tag{7.4}$$

$$A = \sum_n c_n z_\infty^{n-1}$$

As  $\Delta\rho \rightarrow 0$  ( $t \rightarrow \infty$ ),

$$\frac{d \Delta\rho}{dt} \sim - \frac{\Delta\rho}{\tau} \tag{7.5}$$

Using (7.3) and (7.4) in (7.5) and the relation

$$\left( \frac{\partial \rho}{\partial z} \right)_{z=z_\infty} = \sum_n n^2 b_n z_\infty^{n-1} \tag{7.6}$$

one obtains the following relation for the relaxation time:

$$\tau = \left[ \sum_n n^2 b_n(x) z_\infty^n \right] / \left[ \sum_n c_n(x; \kappa) z_\infty^n \right] \tag{7.7}$$

The sum in the numerator of (7.7) is proportional to the isothermal compressibility  $K_T$ ,

$$\sum_n n^2 b_n z_\infty^n = \rho^2 K_T / \beta \tag{7.8}$$

where  $\beta = 1/kT$ . One notes that the rate parameters in (7.7) are contained in the  $c_n$  (through the  $\kappa$  factors).

As one approaches the final density characteristic of a second-order transition (critical point), then  $K_T \rightarrow \infty$  and thus in the limit of internal equilibration  $\tau(T) \rightarrow \infty$  as  $K_T(T) \rightarrow \infty$ . In the magnet the relaxation time varies as the static susceptibility, as shown by Kawasaki.<sup>(7)</sup>

When the final density is a singular point the expansions of (7.3) cannot be used. From the equilibrium theory of critical points one has instead the following variation of  $\Delta z$  with  $\Delta\rho$ :

$$\Delta z \sim (\Delta\rho)^\delta \tag{7.9}$$

[In the magnet, the analog of (7.9) is the variation of the magnetic field  $H$  with magnetization  $M$ :  $H \sim M^\delta$ .] Using (7.9), (7.1) becomes

$$\frac{d \Delta\rho}{dt} \sim -(\Delta\rho)^\delta \tag{7.10}$$

giving

$$\Delta\rho \sim t^{-\nu} \quad (7.11)$$

where

$$\nu = \frac{1}{\delta - 1} \quad (7.12)$$

The quantity  $\delta$  is one of the least well characterized critical exponents. Its value is known exactly only in mean field theory; good estimates are available from analysis of series expansions for the two- and three-dimensional Ising models. The values of  $\delta$  and  $\nu$  are given for several models in Table II.

For some hard-core lattice gases, such as the two-dimensional lattice gas with nearest-neighbor exclusion, analysis of series expansions<sup>(10)</sup> indicates that the singularity at the second-order transition that occurs in these systems is logarithmic, i.e.,

$$K_T \sim \partial\rho/\partial z \sim -\ln \Delta z \quad (7.13)$$

$$\Delta\rho \sim -\Delta z \ln \Delta z \quad (7.14)$$

From (7.14)

$$\frac{d\Delta\rho}{dt} = -(\ln \Delta z) \frac{d\Delta z}{dt} \sim -\Delta z \quad (7.15)$$

or

$$\begin{aligned} (\ln \Delta z)^2 &\sim t \\ \ln \Delta z &\sim -\sqrt{t} \end{aligned} \quad (7.16)$$

Using (7.16) in (7.14) gives the interesting time dependence

$$\Delta\rho \sim \sqrt{t} \exp(-\sqrt{t}) \quad (7.17)$$

Thus, when the final density is the critical density, we can obtain the specific form of the long-time nonexponential behavior in the limit of internal equilibration. We turn now the question of the relation of the limit

**Table II. Values of the Critical Exponent  $\delta$  and the Relaxation Parameter  $\nu$  of (6.23) for Various Models<sup>a</sup>**

Model	$\delta$	$\nu$
Mean field approximation	3	1/2
2D Ising	15	1/14
3D Ising	5	1/4

<sup>a</sup> The values of  $\delta$  are taken from ref. 13. The mean field values apply both to the 2D and 3D Ising models.

of internal equilibration to the opposite limit where internal diffusion is not allowed.

Equation (3.1) gives the general master equation for a lattice system with no internal diffusion, that is, the only transitions included are those that increase or decrease the number of particles. Denoting the transition probabilities of Eq. (3.1) as  $w_e^+$  and  $w_e^-$  representing the exchange of particles with a reservoir, and introducing transition probabilities  $w_d$  for internal diffusion, we obtain the general master equation governing the time evolution of the probability of a lattice configuration  $\gamma_n$  where both exchange and internal diffusion are included:

$$\begin{aligned} \frac{dP(\gamma_n)}{dt} = & \sum_{\gamma_{n-1} \subset \gamma_n} w_e^+(\gamma_{n-1}, \gamma_n) P(\gamma_{n-1}) \\ & - \sum_{\gamma_{n-1} \supset \gamma_n} w_e^-(\gamma_n, \gamma_{n-1}) P(\gamma_n) - \sum_{\gamma_{n+1} \supset \gamma_n} w_e^+(\gamma_n, \gamma_{n+1}) P(\gamma_n) \\ & + \sum_{\gamma_{n+1} \supset \gamma_n} w_e^-(\gamma_{n+1}, \gamma_n) P(\gamma_{n+1}) \\ & + r \left[ \sum_{\gamma'_n \neq \gamma_n} w_d(\gamma'_n, \gamma_n) P(\gamma'_n) - \sum_{\gamma'_n \neq \gamma_n} w_d(\gamma_n, \gamma'_n) P(\gamma_n) \right] \end{aligned} \quad (7.18)$$

The factor  $r$  multiplying the terms describing internal diffusion can be thought of as a charging parameter with which we can turn internal diffusion on and off.

To understand the influence of internal diffusion, it is convenient to express the problem in matrix notation. To this end, we introduce the vector  $\mathbf{p}$ , whose general element is the probability of the  $\gamma_n$ th lattice configuration,  $P(\gamma_n)$ , and the matrices  $\mathbf{W}_e$  and  $\mathbf{W}_d$ ,

$$\begin{aligned} \mathbf{W}_e &= [g(\gamma_m, \gamma_n)] \\ g(\gamma_{n-1}, \gamma_n) &= -w_e^+(\gamma_{n-1}, \gamma_n) \\ g(\gamma_{n+1}, \gamma_n) &= -w_e^-(\gamma_{n+1}, \gamma_n) \\ g(\gamma_n, \gamma_n) &= \sum_{\gamma_{n-1} \subset \gamma_n} w_e^-(\gamma_{n+1}, \gamma_n) + \sum_{\gamma_{n+1} \supset \gamma_n} w_e^+(\gamma_n, \gamma_{n+1}) \\ g(\gamma_{n+m}, \gamma_n) &= 0 \quad (m > 1, m < -1) \\ \mathbf{W}_d &= [h(\gamma'_m, \gamma_n)] \\ h(\gamma'_n, \gamma_n) &= -w_d(\gamma'_n, \gamma_n) \\ h(\gamma_n, \gamma_n) &= \sum_{\gamma'_n \neq \gamma_n} w_d(\gamma_n, \gamma'_n) \\ h(\gamma'_m, \gamma_n) &= 0 \quad (m \neq n) \end{aligned} \quad (7.19)$$

In terms of the quantities  $\mathbf{p}$ ,  $\mathbf{W}_e$ , and  $\mathbf{W}_d$ , (7.18) can be written

$$\frac{d\mathbf{p}}{dt} = -\mathbf{p}\mathbf{W} \quad (7.20)$$

where

$$\mathbf{W} = \mathbf{W}_e + r\mathbf{W}_d \quad (7.21)$$

Neither  $\mathbf{W}_e$  nor  $\mathbf{W}_d$  is symmetric. However, Kawasaki<sup>(7)</sup> has shown that the following matrices are symmetric:

$$\begin{aligned} \mathbf{W}'_e &= \mathbf{P}^{-1/2}\mathbf{W}_e\mathbf{P}^{1/2} \\ \mathbf{W}'_d &= \mathbf{P}^{-1/2}\mathbf{W}_d\mathbf{P}^{1/2} \end{aligned} \quad (7.22)$$

where  $\mathbf{P}$  is a diagonal matrix, the diagonal elements being  $P(\gamma_n)$ . Then

$$\begin{aligned} \mathbf{W} &= \mathbf{P}^{1/2}\mathbf{W}'\mathbf{P}^{-1/2} \\ \mathbf{W}' &= \mathbf{W}'_e + r\mathbf{W}'_d \end{aligned} \quad (7.23)$$

Since the transformations of (7.22) are orthogonal, the eigenvalues of  $\mathbf{W}'$  are the same as those of  $\mathbf{W}$ . The eigenvalues of  $\mathbf{W}'_e$ ,  $\mathbf{W}'_d$ , and  $\mathbf{W}'$  are necessarily nonnegative (otherwise  $\rho \rightarrow \infty$  as  $t \rightarrow \infty$ ). Also, the smallest eigenvalue must be zero to give the steady-state limit. Let  $\lambda_k(\mathbf{W})$  denote the eigenvalues of a general matrix  $\mathbf{W}$ . Then, since  $\mathbf{W}'_e$  and  $\mathbf{W}'_d$  are symmetric nonnegative-definite matrices, it follows that<sup>(11)</sup>

$$\lambda_k(\mathbf{W}'_e + r\mathbf{W}'_d) \geq \lambda_k(\mathbf{W}'_e) \quad (7.24)$$

for all  $k$ . Thus, as we turn on the influence of internal diffusion by increasing  $r$  from zero, all of the eigenvalues increase, i.e., all of the eigenvalues are monotonically increasing functions of  $r$ .

Let  $\lambda_0(r)$  be the smallest nonzero eigenvalue. Then, as  $t \rightarrow \infty$ ,

$$\begin{aligned} \Delta\rho &\sim e^{-\lambda_0(r)t} \\ &\sim e^{-t/\tau} \\ \tau &= \frac{1}{\lambda_0(r)} \end{aligned} \quad (7.25)$$

Thus, when internal diffusion is included, the final relaxation rate is faster

than when there is no internal diffusion.<sup>4</sup> Since all of the eigenvalues become larger as  $r$  is increased, one might conclude that

$$\Delta\rho(t, r > 0) < \Delta\rho(t, r = 0) \tag{7.26}$$

when the initial and final states are the same, that is, that when internal diffusion is included  $\rho$  relaxes to its final value with a faster rate at all times. Although this is generally the case in the numerical examples we have studied, it is not true in all cases, since  $\Delta\rho$  has the general form

$$\Delta\rho = \sum_k A_k e^{-\lambda_k t} \tag{7.27}$$

and it is not necessarily so that

$$A_k(r > 0) < A_k(r = 0) \tag{7.28}$$

An example where the inequality of (7.26) does not hold is the one-dimensional lattice gas with nearest-neighbor attractive interactions with the transition probabilities given by (6.8).

The limit of internal equilibration is simply the limit  $r \rightarrow \infty$ , in which case  $\lambda_0(\infty)^{-1} = \tau$  is given by (7.7). [This limit exists since the internal diffusion reactions in (7.18) do not alter the net density directly; they do alter the  $P(\gamma_n)$  for fixed  $n$  and thereby indirectly influence transitions to  $\gamma_{n-1}$  and  $\gamma_{n+1}$  which of course do alter the density.] Thus, the limit of internal equilibration gives an upper bound to the rate of relaxation at  $t \rightarrow \infty$ ; in most cases it will represent an upper bound for all  $t$ .

In the limit of internal equilibration, if the final density is not a singular point (not a phase transition density), then one can write (5.4) as an expansion about  $\rho_\infty$  (using  $\Delta\rho = \rho_\infty - \rho$ ), giving

$$\begin{aligned} \frac{d \Delta\rho}{dt} &= a_1 \Delta\rho + a_2 (\Delta\rho)^2 + \dots \\ &= a_1 \Delta\rho \left( 1 + \frac{a_2}{a_1} \Delta\rho + \dots \right) \\ &= a_1 \Delta\rho F(\Delta\rho) \end{aligned} \tag{7.29}$$

where  $a_1 = -1/\tau$  and the last equality defines  $F(\Delta\rho)$ . If  $F(\Delta\rho)^{-1}$  is analytic in  $\Delta\rho$ , then (7.29) can be integrated term by term and expressed in the form

$$\sum_{n=1}^{\infty} \alpha_n (\Delta\rho)^n = e^{-t/\tau} \tag{7.30}$$

<sup>4</sup> At constant spin (unlike the exchange process considered here, where the net density changes) Kawasaki<sup>(7)</sup> has shown that the assumption of local equilibrium gives an upper bound for the diffusion of spins. Also see ref. 12.

Inversion of the series gives

$$\Delta\rho = \sum_{n=1}^{\infty} A_n(e^{-t/\tau})^n \quad (7.31)$$

Thus, in the limit of internal equilibration the eigenvalue spectrum is simply  $\lambda_n(r = \infty) = n/\tau$ ,  $\tau$  given by (7.7).

Finally, we note that in the limit of internal equilibration, (5.4) can be written as

$$\frac{d\rho}{dt} = f(\rho, \rho_{\infty}) \quad (7.32)$$

where  $f(\rho, \rho_{\infty})$  is independent of the initial state. Thus,  $d\rho/dt$  at a particular density is the same whether the system starts out at or passes through that density as the system relaxes from the initial to the final state. This means that for a given final state  $\rho_{\infty}$ , there is a universal relaxation curve  $\rho(t)$ . If the assumption of internal equilibration does not hold, Eq. (5.4) still gives the correct first derivative at  $t=0$ . Thus, in the general case the relaxation starts out, from an arbitrary initial density, tangent to the universal relaxation curve, but departs from it at longer times.

## APPENDIX

In this Appendix we give the Mayer coefficients  $c_n(x, u)$  and  $d_n(x, u)$  discussed in Section 4. The interaction parameters  $x$  and  $u$  are illustrated in Fig. 5. Below we give the  $c_n$  through  $n=7$  and the  $d_n$  through  $n=4$  for the plane-square lattice; the coefficients were determined using the technique of Springgate and Poland.<sup>(3)</sup>

$$\begin{aligned} c_1 &= 1, & c_2 &= -5 + 4u, & c_3 &= (31 - 16x) + (-32 + 12x)u + 6u^2 \\ c_4 &= (-209 + 236x - 62x^2) + (236 - 216x + 40x^2)u \\ &\quad + (-62 + 28x + 4x^2)u^2 + 4u^3 \\ c_5 &= (1476 - 2616x + 1450x^2 - 228x^3 - 12x^4) \\ &\quad + (-1744 + 2656x - 1192x^2 + 132x^3 + 8x^4)u \\ &\quad + (524 - 532x + 74x^2 + 24x^3)u^2 + (-48 + 20x + 8x^2)u^3 + u^4 \\ c_6 &= (-10,739 + 26,080x - 22,496x^2 + 7748x^3 - 607x^4 - 112x^5) \\ &\quad + (-13,040 - 28,160x + 20,904x^2 - 5840x^3 + 272x^4 + 64x^5)u \\ &\quad + (-4208 + 6860x - 3022x^2 + 36x^3 + 116x^4 + 8x^5)u^2 \\ &\quad + (444 - 424x - 20x^2 + 56x^3 + 4x^4)u^3 + (-13 + 4x + 4x^2)u^4 \end{aligned} \quad (A.1)$$



$$\begin{aligned}
c_7 = & (79,780 - 246,640x + 291,234x^2 - 158,732x^3 \\
& + 35,424x^4 - 80x^5 - 644x^6 - 32x^7) \\
& + (-98,656 + 277,272x - 291,440x^2 \\
& + 136,932x^3 - 24,392x^4 - 568x^5 + 328x^6 + 20x^7)u \\
& + (33,272 - 75,524x + 56,908x^2 - 13,380x^3 - 1348x^4 + 416x^5 + 76x^6)u^2 \\
& + (-3784 + 5872x - 1696x^2 - 800x^3 + 216x^4 + 52x^5)u^3 \\
& + (127 - 100x - 42x^2 + 24x^3 + 6x^4)u^4 \\
& d_1 = 4, \quad d_2 = -32 + 24u \\
& d_3 = (236 - 92x) + (-248 + 56x)u + (52 + 8x)u^2 \\
& d_4 = (-1744 + 1608x - 344x^2) + (2096x - 1408x + 176x^2)u \\
& \quad + (-648 + 120x + 48x^2)u^2 + (48 + 32x)u^3
\end{aligned} \tag{A.2}$$

In addition, we give the first few terms for the one-dimensional Ising model:

$$\begin{aligned}
c_1 = 1, \quad c_2 = -3 + 2u, \quad c_3 = (10 - 4x) + (-8 + 2x)u + u^2 \\
d_1 = 2, \quad d_2 = -8 + 4u
\end{aligned} \tag{A.3}$$

as well as for the three-dimensional Ising model on the cubic lattice:

$$\begin{aligned}
c_1 = 1, \quad c_2 = -7 + 6u, \quad c_3 = (64 - 36x) + (-72 + 30x)u + 15u^2 \\
d_1 = 6, \quad d_2 = -72 + 60u
\end{aligned} \tag{A.4}$$

For the lattice gas on the square lattice with nearest-neighbor exclusion one has  $c_n = nb_n$ ; the  $b_n$  are known as a byproduct of the Ising series<sup>(4-6)</sup> and are known through  $n = 15$ . We have determined the  $d_n$  through  $n = 7$ , using the technique of Springgate and Poland<sup>(3)</sup>:

$$\begin{aligned}
c_1 &= 1 \\
c_2 &= -5 \\
c_3 &= 31 \\
c_4 &= -209 \\
c_5 &= 1476 \\
c_6 &= -10,739 \\
c_7 &= 79,780
\end{aligned}$$

$$\begin{aligned}
 c_8 &= -601,905 \\
 c_9 &= 4,595,485 \\
 c_{10} &= -35,419,710 \\
 c_{11} &= 275,109,858 \\
 c_{12} &= -2,150,537,435 \\
 c_{13} &= 16,901,814,190 \\
 c_{14} &= -133,452,123,796 \\
 c_{15} &= 1,057,920,031,536
 \end{aligned} \tag{A.5}$$

$$\begin{aligned}
 d_1 &= 4 \\
 d_2 &= -32 \\
 d_3 &= 236 \\
 d_4 &= -1744 \\
 d_5 &= 13,040 \\
 d_6 &= -98,656 \\
 d_7 &= 754,080
 \end{aligned} \tag{A.6}$$

Below we give the series for  $\rho^{(1)}$  and  $\rho^{(2)}$  as functions of the initial density  $\rho_0$  for the plane-square Ising model (letting  $x\kappa = y$ ):

$$\begin{aligned}
 \alpha_0^{(+)} &= 1 \\
 \alpha_1^{(+)} &= -5 + 4y \\
 \alpha_2^{(+)} &= (6 - 12y + 6y^2) + x(4 - 4y) \\
 \alpha_3^{(+)} &= (6 - 8y - 2y^2 + 4y^3) + x(-12 + 32y - 20y^2) + x^2(-4 + 4y^2) \\
 \alpha_4^{(+)} &= (-1 + 16y - 28y^2 + 12y^3 + y^4) + x(-40 + 60y + 8y^2 - 28y^3) \\
 &\quad + x^2(66 - 136y + 62y^2 + 8y^3) \\
 &\quad + x^3(-28 + 52y - 24y^2) + x^4(8 - 8y) \\
 \alpha_5^{(+)} &= (-19 + 64y - 64y^2 + 12y^3 + 7y^4) \\
 &\quad + x(-24 - 112y + 268y^2 - 120y^3 - 12y^4) \\
 &\quad + x^2(282 - 272y - 194y^2 + 180y^3 + 4y^4) \\
 &\quad + x^3(-452 + 592y - 68y^2 - 72y^3) \\
 &\quad + x^4(284 - 332y + 44y^2 + 4y^3) + x^5(-72 + 64y + 8y^2)
 \end{aligned} \tag{A.7}$$

$$\begin{aligned}
\alpha_0^{(-)} &= 0 \\
\alpha_1^{(-)} &= 1 \\
\alpha_2^{(-)} &= 4y + 4x \\
\alpha_3^{(-)} &= (8y + 6y^2) + x(-8 - 20y) + 14x^2 \\
\alpha_4^{(-)} &= (8y + 28y^2 + 4y^3) + x(-8 - 68y - 44y^2) \\
&\quad + x^2(40 + 72y + 4y^2) - 32x^3 - 4x^4 \\
\alpha_5^{(-)} &= (-16y + 76y^2 + 32y^3 + y^4) + x(16 - 48y - 275y^2 - 44y^3) \\
&\quad + x^2(-28 + 216y + 246y^2 + 8y^3) + x^3(28 - 132y - 40y^2) \\
&\quad + x^4(-71 - 24y) - 56x^5
\end{aligned} \tag{A.8}$$

For the same lattice gas with nearest-neighbor exclusion one has

$$\begin{aligned}
\alpha_0^{(+)} &= 1 \\
\alpha_1^{(+)} &= -5 \\
\alpha_2^{(+)} &= 6 \\
\alpha_3^{(+)} &= 6 \\
\alpha_4^{(+)} &= -1 \\
\alpha_5^{(+)} &= -19 \\
\alpha_6^{(+)} &= -42 \\
\alpha_7^{(+)} &= -26 \\
\alpha_8^{(+)} &= 150 \\
\alpha_9^{(+)} &= 626 \\
\alpha_{10}^{(+)} &= 1066 \\
\alpha_{11}^{(+)} &= -690 \\
\alpha_{12}^{(+)} &= -9730
\end{aligned} \tag{A.9}$$

$$\begin{aligned}
\alpha_0^{(-)} &= 0 \\
\alpha_1^{(-)} &= 1 \\
\alpha_n^{(-)} &= 0 \quad (n \geq 2)
\end{aligned} \tag{A.10}$$

For the plane-square Ising model in the limit of internal equilibration one has

$$\begin{aligned}
 \beta_0^{(+)} &= 5 - 4x\kappa \\
 \beta_1^{(+)} &= -12 + 24x\kappa - 12x^2\kappa^2 - 8x + 8x^2\kappa \\
 \beta_2^{(+)} &= -18 + 24x\kappa + 6x^2\kappa^2 - 12k^3\kappa^3 + 36x \\
 &\quad - 96x^2\kappa + 60k^3\kappa^2 + 12x^2 - 12x^4\kappa^2 \\
 \beta_3^{(+)} &= 4 - 64x\kappa + 112x^2\kappa^2 - 48x^3\kappa^3 - 4x^4\kappa^4 \\
 &\quad + 160x - 240x^2\kappa - 32x^3\kappa^2 \\
 &\quad + 120x^4\kappa^3 - 264x^2 + 544x^3\kappa - 248x^4\kappa^2 - 32x^5\kappa^3 + 112x^3 \\
 &\quad - 208x^4\kappa + 96x^5\kappa^2 - 40x^4 + 40x^5\kappa
 \end{aligned} \tag{A.11}$$

$$\begin{aligned}
 \beta_0^{(-)} &= 1 \\
 \beta_1^{(-)} &= -8x + 8x\kappa \\
 \beta_2^{(-)} &= 24x\kappa + 18x^2\kappa^2 - 24x - 60x^2\kappa + 42x^2 \\
 \beta_3^{(-)} &= 32x\kappa + 112x^2\kappa^2 + 16x^3\kappa^3 - 32x \\
 &\quad - 272x^2\kappa - 176x^3\kappa^2 + 160x^2 \\
 &\quad + 288x^3\kappa + 16x^4\kappa^2 - 128x^3 - 16x^4
 \end{aligned} \tag{A.12}$$

In the limit of no internal diffusion the same model gives

$$\begin{aligned}
 \beta_0^{(+)} &= 5 - 4x\kappa \\
 \beta_1^{(+)} &= -12 + 16x\kappa - 4x^2\kappa^2 \\
 \beta_2^{(+)} &= -8 + 2x + 8x\kappa - 40x^2\kappa + 6x^2\kappa^2 + 28x^3\kappa^2 - 12x^3\kappa^3 \\
 &\quad - 8x^4\kappa^3 + 6x^4\kappa^4 \\
 \beta_3^{(+)} &= 16 + 20x - 40x\kappa - 40x^2 - 56x^2\kappa + 56x^2\kappa^2 + 104x^3 + 56x^3\kappa^2 \\
 &\quad - 80x^3\kappa^3 - 100x^4\kappa^2 + 68x^4\kappa^4 + 32x^5\kappa^3 - 20x^5\kappa^4 - 24x^5\kappa^5 \\
 &\quad + 4x^6\kappa^4 + 4x^6\kappa^6
 \end{aligned} \tag{A.13}$$

$$\begin{aligned}
 \beta_0^{(-)} &= 1 \\
 \beta_1^{(-)} &= -8x\kappa + 8x\kappa^2 \\
 \beta_2^{(-)} &= -16x\kappa + 16x\kappa^2 + 20x^2\kappa - 18x^2\kappa^2 - 8x^2\kappa^3 + 6x^2\kappa^4
 \end{aligned}$$

$$\begin{aligned}
\beta_3^{(-)} = & -16x\kappa + 16x\kappa^2 + 64x^2\kappa - 76x^2\kappa^2 \\
& - 16x^2\kappa^3 + 28x^2\kappa^4 - 56x^3\kappa \\
& + 100x^3\kappa^2 - 40x^3\kappa^3 + 16x^3\kappa^4 - 24x^3\kappa^5 \\
& + 4x^3\kappa^6 - 4x^4\kappa^2 - 8x^4\kappa^3 + 12x^4\kappa^4
\end{aligned} \tag{A.14}$$

For the same model in the limit of nearest-neighbor exclusion one has in the limit of internal equilibration

$$\begin{aligned}
\beta_0^{(+)} = 5, & \quad B_0^{(-)} = 1 \\
\beta_1^{(+)} = -12, & \quad \beta_n^{(-)} = 0, \quad (n \geq 1) \\
\beta_2^{(+)} = -18 & \\
\beta_3^{(+)} = 4 & \\
\beta_4^{(+)} = 95 & \\
\beta_5^{(+)} = 252 &
\end{aligned} \tag{A.15}$$

For the same model in the limit of zero internal diffusion one has

$$\begin{aligned}
\beta_0^{(+)} = 5, & \quad \beta_0^{(-)} = 1 \\
\beta_1^{(+)} = -12, & \quad \beta_n^{(-)} = 0 \quad (n \geq 1) \\
\beta_2^{(+)} = -8 & \\
\beta_3^{(+)} = 16 & \\
\beta_4^{(+)} = 64 & \\
\beta_5^{(+)} = 96 &
\end{aligned} \tag{A.16}$$

For the Ising model in one dimension one has in the limit of internal equilibration

$$\begin{aligned}
\beta_0^{(+)} = 3 - 2x\kappa & \\
\beta_1^{(+)} = -2 - 4x + 4x\kappa + 4x^2\kappa - 2x^2\kappa^2 & \\
\beta_0^{(-)} = 1 & \\
\beta_1^{(-)} = -4x + 4x\kappa &
\end{aligned} \tag{A.17}$$

For the same model in the limit of zero internal diffusion one has

$$\begin{aligned}
 \beta_0^{(+)} &= 3 - 2x\kappa \\
 \beta_1^{(+)} &= -2 + 2x^2\kappa^2 \\
 \beta_0^{(-)} &= 1 \\
 \beta_1^{(-)} &= -4x\kappa + 4x\kappa^2
 \end{aligned}
 \tag{A.18}$$

For the three-dimensional Ising model on the cubic lattice in the limit of internal equilibration one has

$$\begin{aligned}
 \beta_0^{(+)} &= 7 - 6x\kappa \\
 \beta_1^{(+)} &= -30 - 12x + 60x\kappa + 12x^2\kappa - 30x^2\kappa^2 \\
 \beta_0^{(-)} &= 1 \\
 \beta_1^{(-)} &= -12x + 12x\kappa
 \end{aligned}
 \tag{A.19}$$

For the same model in the limit of zero internal diffusion one has

$$\begin{aligned}
 \beta_0^{(+)} &= 7 - 6x\kappa \\
 \beta_1^{(+)} &= -30 + 48x\kappa - 18x^2\kappa^2 \\
 \beta_0^{(-)} &= 1 \\
 \beta_1^{(-)} &= -12x\kappa + 12x\kappa^2
 \end{aligned}
 \tag{A.20}$$

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