CSL COORDINATED SCIENCE LABORATORY

ONE-DIMENSIONAL RANDOM WALKS OF LINEAR CLUSTERS

DAVID A. REED
GERT EHRLICH

UNIVERSITY OF ILLINOIS - URBANA, ILLINOIS

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ONE-DIMENSIONAL RANDOM WALKS OF LINEAR CLUSTERS		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER R-718; UILU-ENG 76-2206
7. AUTHOR(s) David A. Reed and Gert Ehrlich		8. CONTRACT OR GRANT NUMBER(s) DMR-72-02937;DAAB-07-72-C-0259
9. PERFORMING ORGANIZATION NAME AND ADDRESS Coordinated Science Laboratory University of Illinois at Urbana-Champaign Urbana, Illinois 61801		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Joint Services Electronics Program		12. REPORT DATE February, 1976
		13. NUMBER OF PAGES 32
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Atom Clusters One-Dimensional Surface Diffusion		

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A stochastic formalism is developed for the one-dimensional surface diffusion of atom clusters, with component atoms located in adjacent channels, by representing the diffusion as a random walk of the center of mass (COM). Relations between the mean square displacement of the center of mass and the rate constants characterizing COM motion are derived for dimers and trimers, starting from the Kolmogorov equation. For dimers in the limit of long diffusion intervals, COM rate constants and individual atomic jump rates can be deduced knowing the mean square displacement and the

20. ABSTRACT (continued)

frequency of occurrence of different dimer configurations. This
analysis is feasible for trimers only under special conditions; even
then, separation into the individual atomic rate processes is not in
general possible.

ONE-DIMENSIONAL RANDOM WALKS
OF LINEAR CLUSTERS

by

David A. Reed and Gert Ehrlich

ONE-DIMENSIONAL RANDOM WALKS OF LINEAR CLUSTERS*

David A. Reed and Gert Ehrlich‡

Coordinated Science Laboratory and

Department of Metallurgy

University of Illinois at Urbana-Champaign

A stochastic formalism is developed for
the one-dimensional surface diffusion of atom
clusters, with component atoms located in
adjacent channels, by representing the diffusion
as a random walk of the center of mass (COM).
Relations between the mean square displacement of
the center of mass and the rate constants charac-
terizing COM motion are derived for dimers and
trimers, starting from the Kolmogorov equation.
For dimers in the limit of long diffusion intervals,
COM rate constants and individual atomic jump rates
can be deduced knowing the mean square displacement
and the frequency of occurrence of different dimer
configurations. This analysis is feasible for
trimers only under special conditions; even then,
separation into the individual atomic rate processes
is not in general possible.

TABLE OF CONTENTS

The routine utilization of the field ion microscope in surface studies has already generated much new information about atomic migration on solids.[1] In such measurements, displacements of individual adatoms are noted for time intervals of length t. The mean square distance covered in one dimension is then related to the diffusion coefficient through Einstein's equation

$$\langle (\Delta R)^2 \rangle = 2Dt \tag{1}$$

for diffusion without drift.[2] There are limits to the accuracy of the determinations set by the statistical nature of the measurements,[3] but these and the underlying formalism are well understood.

Such observations have recently been extended to cover the surface migration of small linear clusters of adatoms, and preliminary measurements of one-dimensional motion at different temperatures are available for several systems.[4-7] Lacking so far, however, is a basis for deriving, from the experimental observations, information about the atomic events in the migration of clusters.

In the diffusion of clusters, Einstein's equation relates the observed displacements to the diffusion coefficient, precisely as with single atoms. However, to maintain correspondence with macroscopic observations of mass transfer in a concentration gradient, the displacements of the center of the mass rather than of the individual adatoms forming the clusters must be measured. There remains a significant problem.

The diffusion coefficient is usually viewed as involving jumps over a barrier of magnitude V_D, and is represented by

- 1 -

$$D = D_0 \exp - V_D/kT \quad . \tag{2}$$

For single adatoms executing a random walk on a lattice of spacing ℓ,

$$\langle (\Delta R)^2 \rangle \equiv \langle (R-\bar{R})^2 \rangle = \Gamma t \ell^2 \quad ; \tag{3}$$

here t is the length of the diffusion interval and Γ the rate at which the atom jumps from one site to another. This is given by

$$\Gamma = \nu \exp - V_D/kT \quad , \tag{4}$$

where ν represents the frequency factor for the diffusive jumps. The prefactor D_0 for one-dimensional motion of single atoms is therefore $D_0 = \nu \ell^2 / 2$, and the barrier derived from an Arrhenius analysis is just that for the individual atomic jumps. For clusters, however, the significance of neither the prefactor D_0 nor the barrier is clear on the atomic level.

In this paper we explore a stochastic formalism relating the diffusion coefficient of linear clusters to the individual atomic events in the overall motion. The presentation will be confined to an analysis of dimers and trimers; these examples already reveal the interesting features of one-dimensional cluster motion, as well as the difficulties of treating higher clusters.

I. OVERALL APPROACH

We consider one-dimensional diffusion on a lattice with spacing ℓ in the direction of motion. The surface cell is presumed symmetrical about two planes normal to the surface, one in the direction of motion and the other at right angles to it. There is only one adatom allowed per

channel; this can jump to an adjacent site, either to the right or to the left of its current position, but never from one channel to another. The adatoms are strongly coupled to their neighbors and clusters never dissociate. As illustrated in Fig. 1 specifically for dimers, adatoms in adjacent rows assume two different configurations. They may be lined up, with the two atoms occupying corresponding sites in their respective rows; alternatively, one atom may be displaced from the other by one site. These configurations have in fact been observed for dimers on the (211) plane of tungsten,[8] and it has been suggested that diffusion occurs in a sequence of single atom jumps,[5] causing the cluster to wiggle along a diffusion channel.

When a dimer changes from one configuration to the other, the location of the center of mass changes by half the surface spacing ℓ. Its motion can therefore be represented as a one-dimensional walk of the center of mass (COM) on a lattice of spacing $\ell/2$, shown in Fig. 2. The individual sites on this lattice will be labeled by the integer x. We assume that the lattice is infinite, so that $-\infty < x < \infty$, and that the random walk always starts in the unit cell based at x = 0. At even sites, the properties of the dimer will in general differ from those at odd sites. The unit cell of the COM lattice is therefore of length ℓ, and has two different points in it. Two rate constants suffice to describe COM movement; jumps from even sites occur at a rate a, from odd sites at a rate b.

For higher clusters, a more general random walk[9] of the center of mass is necessary. In this, the transition probabilities for COM jumps up the lattice, from position x to x + 1, will be denoted by λ_x; for transitions
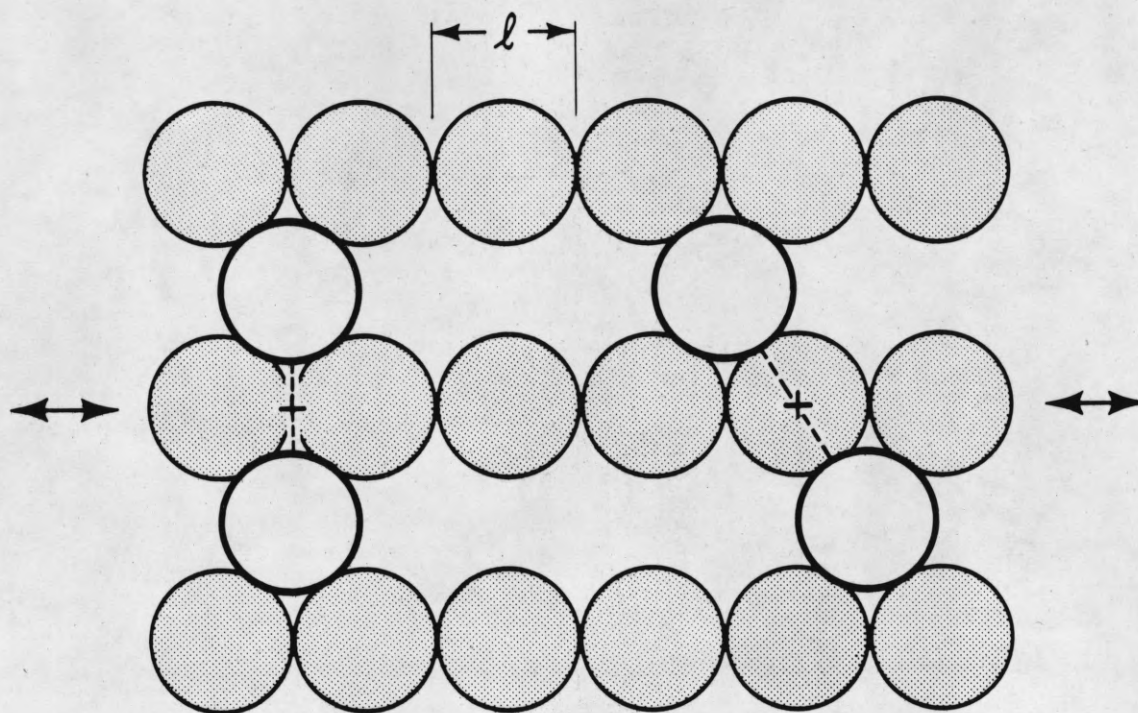
Fig. 1.   Dimer configurations in one-dimensional diffusion. Shading
denotes atoms forming diffusion channels, crosses denote the
location of the center of mass for dimers. Direction of
diffusion is indicated by arrows, surface spacing in this
direction by ℓ.

from x to x - 1 by μ_x. These vary within a unit cell, but are characteristic of the type of the site, as indicated by the appropriate value of x in the unit cell at the origin.

To calculate the mean square displacement in such a random walk, we recall that diffusion on a surface involves transitions continuous in time but between discrete sites.[10] The probability p_x of finding a point x occupied by the center of mass is therefore prescribed by the Kolmogorov equation[11]

$$\frac{dp_x}{dt} = \lambda_{x-1}p_{x-1} - (\lambda_x + \mu_x)p_x + \mu_{x+1}p_{x+1} \tag{5}$$

$$x = 0, \pm 1, \pm 2 \ldots \quad .$$

Multiplying both sides by x^n and then summing over all values of x yields the usual differential equation describing the time evolution of the nth moment[12] of x, $\langle x^n \rangle \equiv \sum_x x^n p_x$:

$$\frac{d\langle x^n \rangle}{dt} = \langle [(x+1)^n - x^n]\lambda_x \rangle - \langle [x^n - (x-1)^n]\mu_x \rangle \quad . \tag{6}$$

Of specific interest is the variance, $\langle (\Delta x)^2 \rangle \equiv \langle x^2 \rangle - \langle x \rangle^2$, for which we have

$$\frac{d\langle (\Delta x)^2 \rangle}{dt} = 2[\langle x\lambda_x \rangle - \langle x\mu_x \rangle - \langle x \rangle(\langle \lambda_x \rangle - \langle \mu_x \rangle)]$$
$$+ [\langle \lambda_x \rangle + \langle \mu_x \rangle] \quad . \tag{7}$$

Implicit in this approach is the assumption that for any COM position x there exists a unique set of two transition probabilities. This condition is satisfied by dimers. For trimers the situation is more

complicated, and as will be seen in Section III, the random walk representation adopted here does not provide a completely general description of the diffusion process.

## II. DIMERS

A. Mean Square Displacements

The unit cell as well as the rate constants for the two COM transitions involved in the motion of dimers are shown in Fig. 2. Changes from a straight to a staggered configuration of the cluster occur at a rate $\underline{a}$. That is, the center of mass moves from point 0 to 1 at a rate $\underline{a}$; it then moves from 1 to 2, or else back to 0, at a different rate $\underline{b}$. With the COM at 1, a pair can have two different but equivalent configurations, illustrated in Fig. 2. It is therefore important to recognize that $\underline{a}$ designates the rate at which changes from 0 to 1 occur, irrespective of the configuration of the dimer in the latter position.

To determine the mean square displacement, we evaluate the quantities entering the right-hand side of Eq. (7). For dimers, the space averaged rate constants for COM motion are

$$\langle \lambda_x \rangle \equiv \sum_x p_x \lambda_x = a P_0^{(z)} + b P_1^{(z)}$$

$$\langle \mu_x \rangle \equiv \sum_x p_x \mu_x = a P_0^{(z)} + b P_1^{(z)} \ . \tag{8}$$

Here $P_i^{(b)}$ denotes the sum of the probabilities p_x taken over all sites of type i; the superscript z explicitly indicates the origin of the walk at time $t = 0$. Thus

$$P_0^{(z)} \equiv \sum_x p_k \qquad k = 0, \pm 2, \pm 4, \ .. \tag{10}$$
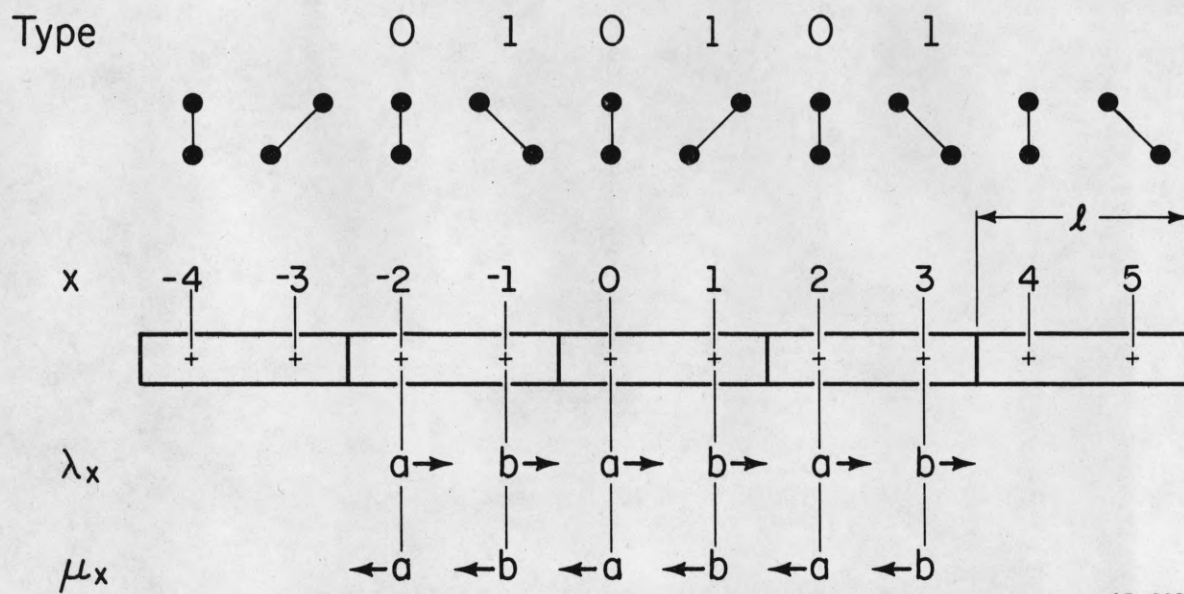
Fig. 2.   Random walk representation of dimer diffusion, showing a sequence of dimer configurations for COM positions x. Unit cell for the representative random walk is indicated by heavy lines. λ_x indicates rate constants for COM transitions to the right, and μ_x to the left.

is the probability of finding the COM at a site of type 0; on the other hand,

$$P_1^{(z)} \equiv \sum_k P_k \qquad k = \pm 1, \pm 3, \ldots \tag{11}$$

represents the probability of having the COM at a site of type 1, irrespective of the particular unit cell. The two must obey the requirement

$$P_0^{(z)} + P_1^{(z)} = 1 . \tag{12}$$

Also,

$$\langle x\lambda_x \rangle \equiv \sum_x x\lambda_x P_x = a\langle x \rangle_0 + b\langle x \rangle_1 \tag{13}$$

$$\langle x\mu_x \rangle \equiv \sum_x x\mu_x P_x = a\langle x \rangle_0 + b\langle x \rangle_1 . \tag{14}$$

Here we have again used the symbol $\langle x \rangle_i$ to denote the average of x over all sites of type i.

Only the last term in Eq. (7) makes a non-vanishing contribution, and the differential equation for the mean square displacement thus reduces to

$$\frac{d\langle (\Delta x)^2 \rangle}{dt} = 2(aP_0^{(z)} + bP_1^{(z)}) . \tag{15}$$

The probability $P_i^{(z)}$ required for solution of Eq. (15) can itself be derived starting from the Kolmogorov equation. Summing Equation (5) over all sites of type 0 gives

$$\frac{dP_0^{(z)}}{dt} = 2(bP_1^{(z)} - aP_0^{(z)}) , \tag{16}$$

and taking advantage of Eq. (12) we find $P_0^{(z)}$ as a function of COM position z at t = 0:

$$P_0^{(0)} = [b + a \ \exp - 2(a+b)t]/(a+b) \tag{17}$$

$$P_0^{(1)} = b[1 - \exp - 2(a+b)t]/(a+b) \tag{18}$$

$$P_1^{(0)} = a[1 - \exp - 2(a+b)t]/(a+b) \tag{19}$$

$$P_1^{(1)} = [a + b \ \exp - 2(a+b)t]/(a+b) \quad . \tag{20}$$

Recalling that at $t = 0$, $\langle (\Delta x)^2 \rangle^{(z)} = 0$, we find the solutions of Eq. (15) are

$$\langle (\Delta x)^2 \rangle^{(0)} = \frac{2a}{a+b} \left\{ 2bt + \frac{(a-b)}{2(a+b)} [1 - \exp - 2(a+b)t] \right\} \tag{21}$$

$$\langle (\Delta x)^2 \rangle^{(1)} = \frac{2b}{a+b} \left\{ 2at - \frac{(a-b)}{2(a+b)} [1 - \exp - 2(a+b)t] \right\} \quad . \tag{22}$$

B. Diffusion Behavior

The mean square displacement of dimers differs from the familiar behavior of single adatoms in at least three ways: it involves two distinct rate constants, does not increase linearly in time, and furthermore depends upon the starting place of the walk.

There are three distinct time regimes in the motion of dimers. For intervals so small that $t \ll [2(a+b)]^{-1}$, Eqs. (21) and (22) reduce to

$$\langle (\Delta x)^2 \rangle^{(0)} = 2 \ at \tag{23}$$

$$\langle (\Delta x)^2 \rangle^{(1)} = 2 \ bt \quad . \tag{24}$$

This linear regime is followed by a transition region with a complicated dependence on the length of the interval. In the other extreme of long time intervals, as $t \to \infty$, the mean square displacement assumes a particularly simple form. It is independent of starting position and linear in time:

$$\langle (\Delta x)^2 \rangle = \frac{4abt}{a+b} \quad . \tag{25}$$

The processes underlying this behavior are evident on examining $P_i^{(z)}$, the probability of finding the COM on a site of type i. If the time interval is short enough, at most a single jump occurs during a diffusion period. The COM is then on a given site only if it started and remained there, or if it started on an adjacent site and made a single jump. The total rate at which the COM leaves a 0 site, going either up or down the lattice, is 2a; it is 2b starting from a 1 site. The probabilities are therefore

$$P_0^{(0)} = 1 - 2at \qquad P_0^{(1)} = 2bt \tag{26}$$

$$P_1^{(0)} = 2at \qquad P_1^{(1)} = 1-2bt \quad , \tag{27}$$

precisely the values given by Eqs. (17)-(20) in the limit $t \ll [2(a+b)]^{-1}$. The mean square displacement under these conditions is just the probability of having made a single jump away from the starting place, and Eqs. (23) and (24) follow immediately. It is interesting to note that for short time intervals, the mean square displacement will be quite different depending upon the origin of the walk, a behavior quite unlike that of

single atoms.

For long diffusion intervals, the different dimer configurations are in local equilibrium. The distributions will remain constant in time provided

$$P_0 a = P_1 b \; . \tag{28}$$

This, together with the requirement that

$$P_0 + P_1 = 1 \tag{29}$$

is of course equivalent to the relations obtained from Eqs. (17)-(20) in the limit $t \gg [2(a+b]^{-1}$, namely[13]

$$P_0 = P_0^{(0)} = P_0^{(1)} = \frac{b}{a+b} \tag{30}$$

$$\lim t \gg [2(a+b)]^{-1}$$

$$P_1 = P_1^{(0)} = P_1^{(1)} = \frac{a}{a+b} \tag{31}$$

$$\lim t \gg [2(a+b)]^{-1} \; .$$

The rate constant describing the approach of $(P_i^{(z)} - P_i)$ to the local equilibrium state appears from Eqs. (17)-(20) as $2(a+b)$. After a time interval $t \gg [2(a+b)]^{-1}$, the probabilities lose all dependence on the starting point, and the initial distribution over the unit cell becomes unimportant. It is this regime which corresponds to large-scale diffusion of dimers, as distinct from the rearrangements within a unit cell that occur during very short time intervals. Only when local equilibrium over the configurations in a unit cell has been established is it therefore proper to relate the mean square displacements to a macroscopic diffusion coefficient.

Averaged over the different positions in an equilibrium distribution, the mean square displacement becomes

$$\langle\langle(\Delta x)^2\rangle\rangle = P_0\langle(\Delta x)^2\rangle^{(0)} + P_1\langle(\Delta x)^2\rangle^{(1)} = \frac{4abt}{a+b} \quad . \tag{32}$$

It must be emphasized that this simple form comes about only through averaging over all starting points. Even when an equilibrium distribution holds, the mean square displacements in Eqs. (21) and (22) may still depend upon starting position whereas the averaged value does not. In the utilization of experimental data, averaging over all starting positions is therefore clearly an advantage.

The significance of the mean square displacement as given by Eq. (32) becomes obvious if we recall Eqs. (30) and (31) to write

$$\langle(\Delta x)^2\rangle = 4P_0 at = 4P_1 bt \quad . \tag{33}$$

From Eq. (8) we know that the total average jump rate is

$$\langle\lambda_x\rangle + \langle\mu_x\rangle = 2(aP_0 + bP_1) = 4aP_0 = 4bP_1 \quad . \tag{34}$$

Just as for an ordinary random walk, the mean square displacement of dimers is therefore given by the product of the total jump rate and the length of the time interval, provided it is averaged over all starting positions in an equilibrium distribution.

C. Atomic Jumps in Diffusion

In actual observations of the mean square distance, only long time intervals are of interest. These are the conditions that correspond to the usual definition of diffusion; they also allow quantitative measurements

over an appreciable range of well defined temperatures. We recall that

for dimers the individual COM displacements are of length $\ell/2$. The actual

mean square distance covered by the COM during a time t becomes, in the

limit $t \gg [2(a+b)]^{-1}$,

$$\langle\langle(\Delta R)^2\rangle\rangle = \frac{ab}{a+b} \, t\ell^2 = P_0 a\ell^2 t = P_1 b\ell^2 t \quad . \tag{35}$$

The mean square distance, and consequently the diffusion

coefficient, is seen to involve contributions from both the rates a and b

which characterize the displacement of the center of mass. Therefore

such a measurement cannot by itself define the individual rate processes

important in the diffusion of the dimer. However, combined observations

of the mean square distance covered during an interval t and of the

occupation probability suffice to define the rate constants entering

the diffusion process. The mean square distance itself also serves as a

convenient indicator to determine if the long time limit has actually

been reached. Local equilibrium will certainly have been established

provided the COM on average samples the entire unit cell. Diffusion measure-

ments should therefore be made for $\langle(\Delta R)^2\rangle/\ell^2 \geq 1$.

It must be emphasized that the rate constants a and b

refer to COM motion throughout. Specifying the site specifies

the configuration of the dimer only if it is at a 0 site; on a 1

position two configurations contribute equally. As in Eq. (4), we write

the rate of an atomic jump as the product of a frequency factor ν and a

Boltzmann term involving the activation energy $E^{\ddagger}$; we therefore have

$$\underline{a} = 2\nu_a \exp - E_a^{\ddagger}/kT$$

$$\underline{b} = \nu_b \exp - E_b^{\ddagger}/kT \quad . \tag{36}$$

One final question remains: can the mean square distance and the occupation probabilities be determined accurately enough to derive significant values of the rate constants for COM motion? Consider systems for which $P_0 > P_1$; the opposite case is equivalent. Inasmuch as $P_1 = 1 - P_0$, the standard deviation $\sigma(\underline{a})$ of the rate constant $\underline{a}$ follows, from the usual rules for the propagation of errors[14] due to independent variables, as

$$\frac{\sigma(a)}{a} = \{\sigma^2 [\langle\langle(\Delta R)^2\rangle\rangle]/\langle\langle(\Delta R)^2\rangle\rangle^2 + \sigma^2(P_0)/P_0^2\}^{\frac{1}{2}} \quad . \tag{37}$$

The relative error in the mean square distance has been estimated from Monte Carlo simulations.[3] Provided one hundred separate diffusion intervals are observed, the standard error amounts to $\approx 15\%$ of $\langle\langle(\Delta R)^2\rangle\rangle$. As shown in Appendix A, the relative error in P_0, based on a total of M observations, is

$$\frac{\sigma(P_0)}{P_0} = \left[\frac{1}{(M-1)} \frac{P_1}{P_0}\right]^{\frac{1}{2}} \quad . \tag{38}$$

Again for one hundred observations the relative error in P_0 at most amounts to 10%. It is therefore clear that in the linear diffusion of dimers, statistically significant values of the atomic jump rates can be achieved without special effort, provided observations of the mean square distance and the occupation probabilities are available.
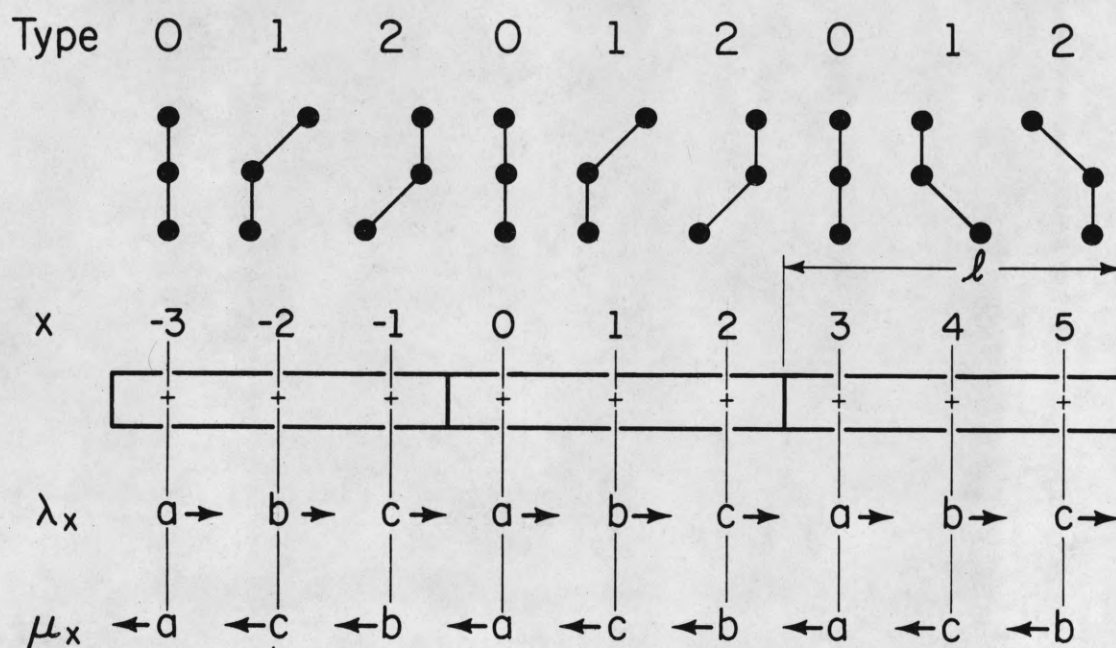
III. DIFFUSION OF TRIMERS

For a trimer the displacement of any one adatom changes the COM position by $\ell/3$, and this will serve as the new unit of length for the representative random walk. A typical sequence of atomic arrangements for a moving trimer is shown in Fig. 3. The unit cell of the one-dimensional lattice appropriate to this sequence has three sites in it, labeled 0, 1, and 2. Three rate constants a, b, and c define COM motion. However, this is only part of the story.

For trimers, there is another, energetically different, configuration possible at each of the sites. In the actual diffusion process, sequences involving these alternate configurations may participate to a significant, and perhaps even dominant extent. The diffusion of trimers therefore cannot be discussed in its full generality using the random walk representation so useful for dimers. In outlining a formalism for diffusion we restrict ourselves to a particularly simple model of trimer motion. We assume that diffusion occurs by a symmetrical sequence of atomic arrangements, such as shown in Fig. 3. Even this simple model, the consequences of which are worked out in the following pages, serves to demonstrate the complicated diffusion behavior for trimers, a behavior that defies general analysis.

A. Mean Square Displacements

In order to describe the mean square displacement of trimers diffusing in conformity with our model, we proceed as we did for dimers to solve the differential equation (7). The position averaged rate

Fig. 3.   Representation of trimer diffusion. One particular, symmetrical
sequence of configurations involved in the diffusion is shown
at the top, together with the type of site. The unit cell, and
the COM rate constants λ_x and μ_x to represent diffusion occurring
via this sequence, are given below.

constants for trimers are

$$\langle \lambda_x \rangle = aP_0^{(z)} + bP_1^{(z)} + cP_2^{(z)} \tag{39}$$

$$\langle \mu_x \rangle = aP_0^{(z)} + cP_1^{(z)} + bP_2^{(z)} \quad . \tag{40}$$

The probabilities $P_i^{(z)}$ of the COM being at a site of type i, having started at z, are now related through

$$P_0^{(z)} + P_1^{(z)} + P_2^{(z)} = 1 \quad . \tag{41}$$

Also we have

$$\langle x\lambda_x \rangle = a\langle x \rangle_0 + b\langle x \rangle_1 + c\langle x \rangle_2 \tag{42}$$

$$\langle x\mu_x \rangle = a\langle x \rangle_0 + c\langle x \rangle_1 + b\langle x \rangle_2 \quad . \tag{43}$$

All the terms in Eq. (7) now contribute and we find

$$\frac{d\langle (\Delta x)^2 \rangle}{dt} = 2(b-c)[\langle x \rangle_1 - \langle x \rangle_2 + \langle x \rangle(P_2^{(z)} - P_1^{(z)})] + P_0^{(z)}(2a-b-c) + b + c \quad . \tag{44}$$

By summing the Kolmogorov equation alternately over sites of type 2 and 1 we get

$$\frac{d(P_2^{(z)} - P_1^{(z)})}{dt} = - (2b+c)(P_2^{(z)} - P_1^{(z)}) \quad . \tag{45}$$

Using the appropriate boundary conditions, this immediately leads to

$$P_2^{(0)} - P_1^{(0)} = 0 \tag{46}$$

$$P_2^{(1)} - P_1^{(1)} = - \exp - (2b+c)t \tag{47}$$

$$P_2^{(2)} - P_1^{(2)} = \exp - (2b+c)t \quad . \tag{48}$$

With these results and the differential equation for $P_0^{(z)}$ derived from Eq. (5),

$$\frac{dP_0^{(z)}}{dt} = c(P_2^{(z)} + P_1^{(z)}) - 2aP_0^{(z)} \quad , \tag{49}$$

we find

$$P_0^{(0)} = [c + 2a \exp - (2a + c)t]/(2a + c) \tag{50}$$

$$P_0^{(1)} = c[1 - \exp - (2a + c)t]/(2a + c) \tag{51}$$

$$P_0^{(2)} = c[1 - \exp - (2a + c)t]/(2a + c) \quad . \tag{52}$$

We still require information about $\langle x \rangle$ as well as about $\langle x \rangle_1 - \langle x \rangle_2$. It follows from Eq. (6) that

$$\frac{d\langle x \rangle}{dt} = \langle \lambda_x \rangle - \langle \mu_x \rangle = (b-c)(P_1^{(z)} - P_2^{(z)}) \quad , \tag{53}$$

and therefore

$$\langle x \rangle^{(0)} = 0 \tag{54}$$

$$\langle x \rangle^{(1)} = [3b - (b-c) \exp - (2b + c)t]/(2b + c) \tag{55}$$

$$\langle x \rangle^{(2)} = [3(b+c) + (b-c)\exp - (2b + c)t]/(2b + c) \quad . \tag{56}$$

Multiplying Kolmogorov's equation by x^n, and then summing over all sites of a given type i, we obtain the differential equation for $\langle x^n \rangle_i$:

$$\frac{d\langle x^n \rangle_i}{dt} = [\langle (x+1)^n \lambda_x \rangle_{i-1} - \langle x^n \lambda_x \rangle_i] - [\langle x^n \mu_x \rangle_i - \langle (x-1)^n \mu_x \rangle_{i+1}] \quad . \tag{57}$$

This immediately leads to the last relation required,

$$\frac{d(\langle x \rangle_1 - \langle x \rangle_2)}{dt} = -(2b+c)(\langle x \rangle_1 - \langle x \rangle_2) + (2a+b)P_0^{(z)} - b \quad . \tag{58}$$

Keeping in mind the distinct boundary conditions for the different starting positions, we find

$$(\langle x \rangle_1 - \langle x \rangle_2)^{(0)} = \frac{2a}{2a+c} \left\{ \frac{(c-b)}{2b+c} [1-\exp-(2b+c)t] - \frac{(2a+b)}{2(a-b)} [\exp-(2a+c)t \right.$$
$$\left. - \exp-(2b+c)t] \right\} \tag{59}$$

$$(\langle x \rangle_1 - \langle x \rangle_2)^{(1)} = \frac{1}{2a+c} \left\{ \frac{2a(c-b)}{2b+c} [1-\exp-(2b+c)t] + \frac{c(2a+b)}{2(a-b)} \times \right.$$
$$\left. [\exp-(2a+c)t - \exp-(2b+c)t] \right\} + \exp-(2b+c)t \tag{60}$$

$$(\langle x \rangle_1 - \langle x \rangle_2)^{(2)} = \frac{1}{2a+c} \left\{ \frac{2a(c-b)}{2b+c} [1-\exp-(2b+c)t] + \frac{c(2a+b)}{2(a-b)} \times \right.$$
$$\left. [\exp-(2a+c)t - \exp-(2b+c)t] \right\} - 2\exp-(2b+c)t \quad . \tag{61}$$

The mean square displacement can now be obtained directly from differential equation (44):

$$\langle (\Delta x)^2 \rangle^{(0)} = \frac{2a}{2a+c} \left\{ \frac{9bct}{2b+c} + \frac{3b(b-c)(2a+c)}{(a-b)(2b+c)^2} [1-\exp-(2b+c)t] \right.$$
$$\left. + \frac{[(a-b)(2a+b)-(a-b)(2b+c)-(b-c)(2a+b)]}{(a-b)(2a+c)} [1-\exp-(2a+c)t] \right\} \tag{62}$$

$$\langle (\Delta x)^2 \rangle^{(1)} = \langle (\Delta x)^2 \rangle^{(2)} = \frac{1}{2a+c} \left\{ \frac{18\,abct}{2b+c} - \frac{3bc(b-c)(2a+c)}{(a-b)(2b+c)^2} [1-\exp-(2b+c)t] \right.$$
$$- \frac{c[(a-b)(2a+b)-(a-b)(2b+c)-(b-c)(2a+b)]}{(a-b)(2a+c)} [1-\exp-(2a+c)t]$$
$$\left. + \frac{(b-c)^2(2a+c)}{(2b+c)^2} [1-\exp-2(2b+c)t] \right\} \quad . \tag{63}$$

B. Diffusion of Model Trimers

Despite its greater complexity, the mean square displacement for the trimer configurations considered here is similar to that of dimers in its overall dependence upon the length of the diffusion interval. At very short times, the mean square displacement is linear in t; this regime is not of particular interest. In the opposite extreme of long times, an equilibrium distribution is set up over the unit cells and the mean square displacement again assumes a simpler form.

For these trimers two different decay times characterize the approach to local equilibrium. This is apparent from the probabilities $P_i^{(z)}$ of finding the COM on a site of type i after starting at z. The probabilities derived from Eqs. (41) and (46) - (52) are

$$P_0^{(0)} = [c + 2a \ exp-(2a+c)t]/(2a+c) \tag{50}$$

$$P_0^{(1)} = c[1-exp-(2a+c)t]/(2a+c) = P_0^{(2)} \tag{51-52}$$

$$P_1^{(0)} = a[1-exp-(2a+c)t]/(2a+c) = P_2^{(0)} \tag{64}$$

$$P_1^{(1)} = [2a+c \ exp-(2a+c)t + (2a+c)exp-(2b+c)t]/[2(2a+c)] = P_2^{(2)} \tag{65}$$

$$P_1^{(2)} = [2a+c \ exp-(2a+c)t-(2a+c)exp-(2b+c)t]/[2(2a+c)] = P_2^{(1)} . \tag{66}$$

The rate constant at which $P_0^{(z)}$ reaches its asymptotic limit is (2a +c); (2b +c) describes the rate of change of $P_2^{(z)} - P_1^{(z)}$ for z = 1 or 2. During time intervals long enough for local equilibrium to be established,

these probabilities become independent of starting point z. This asymptotic limit is achieved only for t large compared to both $(2a+c)^{-1}$ and $(2b+c)^{-1}$. In this limit, which is the one of primary experimental interest, we have the three relations

$$P_0 = \frac{c}{2a+c} \qquad P_1 = \frac{a}{2a+c} = P_2 \; . \tag{67}$$

It is interesting to note that sites of type 1 and 2, which in our model are energetically equivalent, have identical probabilities in the limit of long times. Also, $(\langle x \rangle_1 - \langle x \rangle_2)^{(z)}$ assumes a value

$$\langle x \rangle_1 - \langle x \rangle_2 = \frac{2a(c-b)}{(2a+c)(2b+c)} \tag{68}$$

independent of the origin of the walk.

In order to relate the mean square displacement directly to experiment, we average the quantities given by Eqs. (62) and (63) over the different starting places. For diffusion intervals during which the distribution achieves local equilibrium, this averaged mean square displacement is

$$\langle \langle (\Delta x)^2 \rangle \rangle = \frac{2a}{(2a+c)(2b+c)} \left\{ 9bct + \frac{(b-c)^2}{2b+c} [1-\exp-2(2b+c)t] \right\} \; . \tag{69}$$

In the limit of very long times, the mean square distance then becomes

$$\langle \langle (\Delta R)^2 \rangle \rangle = \frac{2\ abct\ \ell^2}{(2a+c)(2b+c)} \; . \tag{70}$$

This form is not necessarily achieved once an equilibrium distribution is reached. It requires that $t \gg (b-c)^2/[9bc(2b+c)]$, quite unlike the situation for dimers. Also, for dimers the mean square distance is directly proportional to the mean jump rate $\langle \lambda_x \rangle + \langle \mu_x \rangle$. For trimers in an equilibrium distribution,

$$\langle \lambda_x \rangle + \langle \mu_x \rangle = \frac{2a(2c+b)}{(2a+c)} \quad , \tag{71}$$

and there appears no simple relation between the jump rate and the mean square distance. A unified interpretation for dimers as well as trimers is possible, however, in terms of the transit time τ, the average time spent by the COM in spanning the length of a unit cell. This quantity is evaluated separately in Appendix C, and in the limit of long diffusion intervals

$$\langle \langle (\Delta R)^2 \rangle \rangle = t \ell^2 / \tau \quad . \tag{72}$$

The ratio t/τ gives the rate at which the distance ℓ is traversed, and to that extent the usual form for the mean square distance in a random walk is preserved for trimers.

C. Analysis of Diffusion Experiments

All three rate constants a, b, and c enter into the diffusion coefficient of trimers migrating in conformity with our model. Clearly a measurement of the mean square distance does not by itself suffice to define these constants. Analysis of the individual steps is aided by data derived from the distribution of the COM over different kinds of sites. Using Eq. (67) for the occupation probabilities in the asymptotic limit, it proves advantageous to write the mean square distance as

$$\langle \langle (\Delta R)^2 \rangle \rangle = \frac{2a P_0 t \ell^2}{2+c/b} = \frac{2b P_1 t \ell^2}{1+2b/c} \quad . \tag{73}$$

The problem now is to assign an order of magnitude to the ratio b/c. In principle this can be done by measuring the quantity $\langle \Delta_{12} \rangle \equiv \langle x \rangle_1 - \langle x \rangle_2$; once local equilibrium is achieved, we know from Eqs. (67) and (68) that

$$\langle \Delta_{12} \rangle = 2P_1(1-b/c)/(1+2b/c) \quad . \tag{74}$$

The question arises whether or not b/c can be determined accurately enough from measurements of P_1 and $\langle \Delta_{12} \rangle$. The standard error of b/c is

$$\sigma(b/c) = \frac{3}{2(P_1 + \langle \Delta_{12} \rangle)^2} [\langle \Delta_{12} \rangle^2 \sigma^2(P_1) + P_1^2 \sigma^2(\langle \Delta_{12} \rangle)]^{\frac{1}{2}} . \qquad (75)$$

As shown in Appendix A, the standard error of P_1 estimated from M observations is given by

$$\hat{\sigma}(P_1) = \left[\frac{P_1}{M-1} (1-P_1) \right]^{\frac{1}{2}} . \qquad (76)$$

The error in $\langle \Delta_{12} \rangle$, derived in Appendix B, is

$$\sigma(\langle \Delta_{12} \rangle) \sim \left[\frac{2}{M} \langle \langle (\Delta x)^2 \rangle \rangle \right]^{\frac{1}{2}} . \qquad (77)$$

Since the mean square distance varies linearly with time t, it appears advantageous to operate over diffusion intervals as short as consistent with achieving local equilibrium, with as many observations as feasible, in order to reduce the error in $\langle \Delta_{12} \rangle$. The relative error in b/c expected for different values of the rate constants a, b, and c is shown in Figure 4. It is clear that only for P_1 large, when the probability of finding the center of mass on a site of type 1 or 2 is high, can a useful analysis of COM jump rates be attempted for trimer diffusion. Even then it is desirable that b/c < 1; the error in determining this ratio from observed values of $\langle \Delta_{12} \rangle$ and P_1 may otherwise be excessive. That these conditions are satisfied can be established from the experimental results. If they are met, the combined observation of the mean square distance $\langle \langle (\Delta R)^2 \rangle \rangle$, of the distribution over different sites, specifically P_1, and of $\langle \Delta_{12} \rangle = \langle x \rangle_1 - \langle x \rangle_2$ suffices to define the COM rate constants a and c and to give an order of magnitude for the value of b.
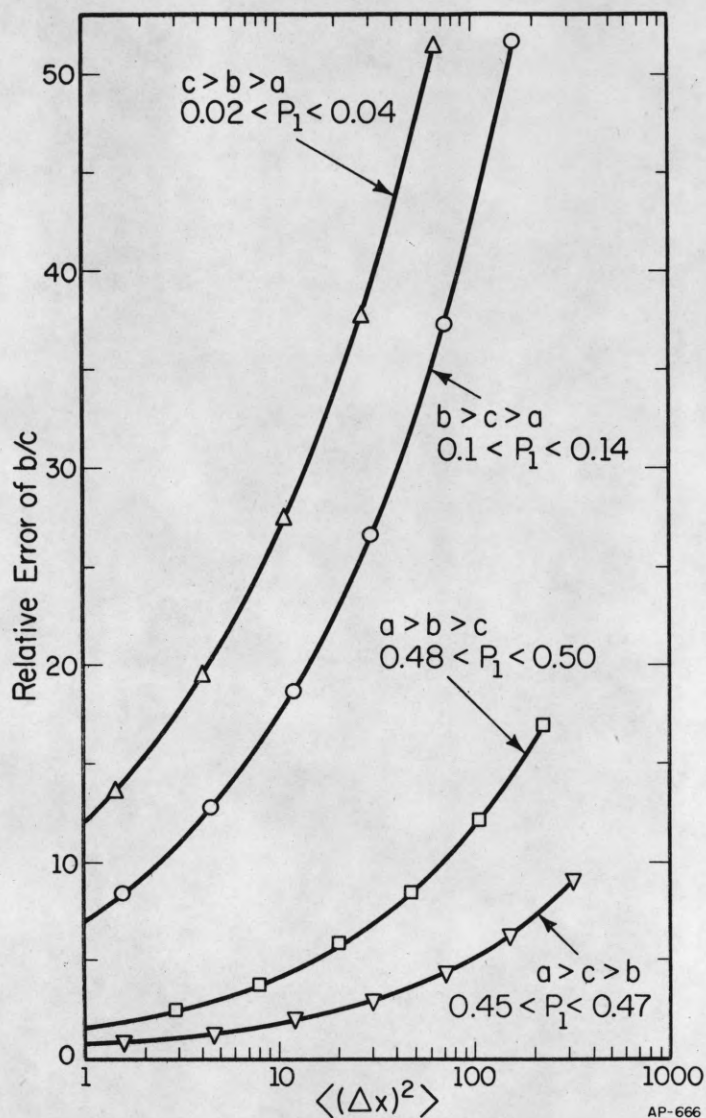
Fig. 4.   Relative error in b/c as a function of the mean square displacement. All values for 100 observations, a diffusion interval t of 100 sec, $v_a = 15 \times 10^9 \text{ sec}^{-1}$, $v_b = v_c = 10^{10} \text{ sec}^{-1}$.

$c > b > a$: $E_a^{\ddagger} = 15$ kcal/mole, $E_b^{\ddagger} = 14$, $E_c^{\ddagger} = 13$.

$b > c > a$:   15   13   14.

$a > b > c$:   13   14   15.

$a > c > b$:   13   15   14.

$P_1 = [2 + \exp(E_a^{\ddagger} - E_c^{\ddagger})/kT]^{-1}$.

D. Atomic Jump Rates and Trimer Diffusion

The analysis so far has been confined to a particular model of trimer diffusion, in which three rate constants serve to describe COM movement. As has already been stressed, the actual diffusion process is likely to be much more complicated. For trimers, nine distinct atomic jump processes can be identified in one-dimensional diffusion. These and the different atomic arrangements involved are defined in Fig. 5. Configurations in which the trimer is V-shaped or slanted are labeled by the superscript B, the others by the superscript A. Subscripts denote the three different types of jumps possible from any one COM position.

In view of the difficulties encountered in analysing diffusion even for our simple model, we eschew a complete examination of the actual atomic events. To consider the diffusion of real trimers, for which the limited sequence of configurations in Fig. 3 may not be strictly applicable, we restrict ourselves to systems for which local equilibrium prevails,[15] and assume that the rate constants $\underline{a}$, $\underline{b}$, and $\underline{c}$ can be treated as averages. Provided the relative probabilities of finding different configurations at a given site conform to the equilibrium values, then these average rate constants are related to the atomic jump processes[16] through

$$\underline{a} = \frac{1}{P_0} \left(P_0^A a_I + P_0^A a_{II} + P_0^B a_{III} \right) \tag{78}$$

$$\underline{b} = \frac{1}{P_1} \left(P_1^A b_I + P_1^A b_{II} + P_1^B b_{III} \right) \tag{79}$$

$$\underline{c} = \frac{1}{P_2} \left(P_2^A c_I + P_2^A c_{II} + P_2^B c_{III} \right) . \tag{80}$$
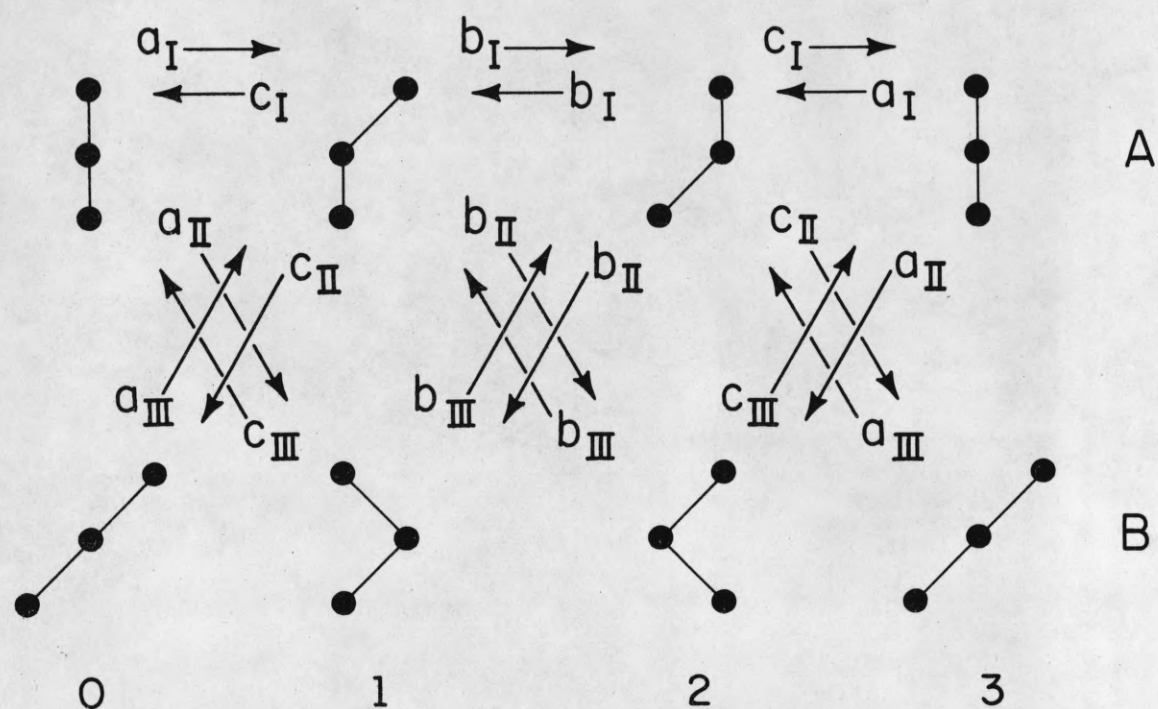
Fig. 5.   Atomic configurations and rate constants for one-dimensional
motion of trimers. COM sites indicated by numerals. A and B
distinguish the two energetically nonequivalent configurations
possible at each site.

Not all the atomic jump rates are independent. The requirements of detailed balance in an equilibrium ensemble yield connections between the jump rates and the probabilities of observing differently configured trimers:

$$\frac{P_0^A}{P_I^A} = \frac{c_I}{a_I} = \frac{P_0^A}{P_2^A} \tag{81}$$

$$\frac{P_0^A}{P_1^B} = \frac{c_{III}}{a_{II}} = \frac{P_0^A}{P_2^B} \tag{82}$$

$$\frac{P_0^B}{P_1^A} = \frac{c_{II}}{a_{III}} = \frac{P_0^B}{P_2^A} \tag{83}$$

and finally

$$\frac{P_1^B}{P_2^A} = \frac{b_{II}}{b_{III}} \ . \tag{84}$$

These can be combined to give the relative occurrence of different configurations on sites of the same type:[17]

$$\frac{P_0^A}{P_0^B} = \frac{a_{III}c_I}{a_I c_{II}} \tag{85}$$

and

$$\frac{P_1^A}{P_1^B} = \frac{a_I c_{III}}{a_{II} c_I} \ . \tag{86}$$

If the individual jump rates are all known, these relations allow us to evaluate the average rate constants for the center of mass.

The inverse, deduction of the rate-limiting jump process from a knowledge of the COM rates $\underline{a}$, $\underline{b}$, and $\underline{c}$ and the observed equilibrium ratios (81) - (84), is not generally possible. Nevertheless, the probabilities of finding trimers in different configurations, observed as a function of temperature, can yield the differences in internal energy between these configurations. This may, indirectly, help in the analysis of the diffusion events.

IV. CONCLUSIONS

Only clusters of three atoms or less have been considered. For larger linear clusters, such as tetramers, the atomic jumps involved in linear diffusion are more numerous but not essentially different. The problems in examining the details of the diffusion process are much the same as those already noted for trimers.

It appears that from the formalism developed here for clusters it is not generally possible to unequivocally sort out the rates of individual atomic jumps from the observed values of the mean square displacement. Only for dimers can the rate-limiting jump process always be established. A knowledge of the mean square distance, combined with measurements of the relative probabilities of finding dimers in the two configurations available to them, suffices to define the atomic processes in linear diffusion. Under special circumstances a complete analysis of the motion of the center of mass is possible for higher clusters as well, even though individual atomic jumps cannot be isolated quantitatively. Additional information may, however, yield further insights into the individual rate processes important in the diffusion of such clusters. Especially interesting should be comparisons of the diffusion parameters

for differently sized clusters, and information about the probability of occurrence of various cluster configurations. The latter is, in any event, important for a better understanding of atomic interactions at a surface.

APPENDIX A: THE STANDARD ERROR IN P_i

In order to measure P_i, we make M observations in which the state of occupation of sites of type i is noted. If such a site is occupied, we assign a value of 1 to the occupation variable ρ; otherwise ρ is set equal to zero. Therefore

$$P_i = \frac{1}{M} \sum_{k=1}^{M} \rho_k \tag{A1}$$

and

$$\text{var } P_i = \frac{1}{M^2} \text{var} \sum_{k=1}^{M} \rho_k \ . \tag{A2}$$

We can arrive at an estimate,[14] $\hat{\text{var}} \ \rho_k$, for the variance of any single measurement of the occupation variable, from

$$\hat{\text{var}} \ \rho_k = \frac{M}{M-1} \left[\frac{\sum_k \rho_k^2}{M} - \left(\frac{\sum_k \rho_k}{M} \right)^2 \right] \ . \tag{A3}$$

Inasmuch as ρ can only assume values of either 0 or 1,

$$\sum_k \rho_k = MP_i = \sum_k \rho_k^2 \tag{A4}$$

and

$$\hat{var} \, \rho_k = \frac{MP_i}{M-1} (1-P_i) \quad . \tag{A5}$$

Finally, since the variance of a sum of independent quantities is just the sum of the individual variances,

$$\hat{var} \, P_i = \frac{P_i}{M-1} (1-P_i) \quad . \tag{A6}$$

APPENDIX B: THE STANDARD ERROR OF $\langle \Delta_{12} \rangle$ FOR TRIMERS

To evaluate $var \langle \Delta_{12} \rangle$ in the limit $t \rightarrow \infty$, note that $\Delta_{12} \equiv x_1 - x_2$, and that

$$var \, \Delta_{12} = (\langle x^2 \rangle_1 + \langle x^2 \rangle_2) - (\langle x \rangle_1^2 + \langle x \rangle_2^2) \quad . \tag{B1}$$

The terms at the extreme right can be found by taking advantage of the fact that

$$\langle x \rangle_0 + \langle x \rangle_1 + \langle x \rangle_2 = \langle x \rangle \quad . \tag{B2}$$

From Eq. (57) we know that

$$\frac{d\langle x \rangle_0}{dt} = c(\langle x \rangle_2 + \langle x \rangle_1) - 2a\langle x \rangle_0 + c(P_2 - P_1) \quad . \tag{B3}$$

Eq. (B3) together with the expression for $\langle x \rangle_1 - \langle x \rangle_2$ from (68) now yields the following values for $\langle x \rangle_i$:

$$\langle x \rangle_0^{(0)} = 0 \qquad \langle x \rangle_1^{(0)} = \frac{a(c-b)}{(2a+c)(2b+c)} \qquad \langle x \rangle_2^{(0)} = -\frac{a(c-b)}{(2a+c)(2b+c)}$$

$$\tag{B4}$$

$$\langle x \rangle_0^{(1)} = \frac{3bc}{(2a+c)(2b+c)} \qquad \langle x \rangle_1^{(1)} = \frac{a}{(2a+c)} \qquad \langle x \rangle_2^{(1)} = \frac{a(4b-c)}{(2a+c)(2b+c)}$$

$$\text{(B5)}$$

$$\langle x \rangle_0^{(2)} = \frac{3c(b+c)}{(2a+c)(2b+c)} \qquad \langle x \rangle_1^{(2)} = \frac{2a(2c+b)}{(2a+c)(2b+c)} \qquad \langle x \rangle_2^{(2)} = \frac{2a}{(2a+c)} \; .$$

$$\text{(B6)}$$

The quantities in the first parenthesis on the right-hand side of Eq. (B1) are immediately accessible from differential equation (57). Substituting values for P_0, P_1, and $\langle \Delta_{12} \rangle$ from Eqs. (67) and (68), we find, on neglecting constant terms by comparison with those depending on t, that

$$\text{var } \Delta_{12} \sim \frac{2a}{(2a+c)} \; \frac{18abct}{(2a+c)(2b+c)} \; . \qquad \text{(B7)}$$

The quantity of interest is actually var $\langle \Delta_{12} \rangle$, the variance of an average value of Δ_{12} obtained from many observations. Assume that M individual observations have been made of the displacement of the COM. Of these only MxP_1 will have terminated on either a 1 or 2 site, and therefore

$$\text{var } \langle \Delta_{12} \rangle \sim \frac{2a+c}{aM} \text{ var } \Delta_{12} = \frac{2}{M} \langle \langle (\Delta x)^2 \rangle \rangle \; . \qquad \text{(B8)}$$

APPENDIX C: THE TRANSIT TIME τ

Consider initially the average time τ_i required for the COM to reach, for the first time, either of two points, arbitrarily chosen as $x = 0$ and $x = L$; the COM starts at $x = i$, where $0 < i < L$, and once either of the limiting positions is reached, we consider the random walk over. The times τ_i are governed by the simple recursion relation[11]

$$\tau_i = \frac{1}{\lambda_i + \mu_i} + \frac{\lambda_i}{\lambda_i + \mu_i} \tau_{i+1} + \frac{\mu_i}{\lambda_i + \mu_i} \tau_{i-1} \qquad 0 < i < L \ , \qquad (C1)$$

where the mean time spent at any point i is $(\lambda_i + \mu_i)^{-1}$. Eq. (C1) can be rearranged to give

$$\tau_i - \tau_{i+1} = \frac{1}{\lambda_i} + \frac{\mu_i}{\lambda_i} (\tau_{i-1} - \tau_i) \ . \qquad (C2)$$

Making use of the condition $\tau_0 = \tau_L = 0$, we find, by repeated substitution for $(\tau_{i-1} - \tau_i)$ in Eq. (C2) until $i = 1$, that

$$\tau_i - \tau_{i+1} = \sum_{j=1}^{i} \frac{1}{\lambda_j} \prod_{k=j+1}^{i} \frac{\mu_k}{\lambda_k} - \tau_1 \prod_{k=1}^{i} \frac{\mu_k}{\lambda_k} \ , \qquad (C3)$$

where we set $\prod_{i+1}^{i} \frac{\mu_k}{\lambda_k} = 1$. This series of equations can be solved to give

$$\tau_i = A_i - B_i \left[\frac{1 + \lambda_1 A_2}{\mu_1 + \lambda_1 (1 + B_2)} \right] \ , \qquad (C4)$$

with

$$A_i \equiv \sum_{m=i}^{L-1} \sum_{j=1}^{m} \frac{1}{\lambda_j} \prod_{k=j+1}^{m} \frac{\mu_k}{\lambda_k} \qquad (C5)$$

and

$$B_i \equiv \sum_{m=i}^{L-1} \prod_{k=1}^{m} \frac{\mu_k}{\lambda_k} \quad . \tag{C6}$$

We now define the transit time τ as the mean time for the COM to move from one position to its counterpart in either of the neighboring unit cells. For dimers, the transit time, obtained from Eqs. (C4)-(C6) by letting $i = 2$ and $L = 4$, is

$$\tau = (a+b)/ab \quad . \tag{C7}$$

For trimers diffusing as in Fig. 3, substitution of $i = 3$ and $L = 6$ gives

$$\tau = (2a+c)(2b+c)/2abc \quad , \tag{C8}$$

independent of starting point.

1. For a recent review, see W. R. Graham and G. Ehrlich, Thin Solid Films 25, 85 (1975).

2. Atomic processes in diffusion are examined by J. R. Manning, Diffusion Kinetics for Atoms in Crystals (Van Nostrand, Princeton, N.J., 1968).

3. D. A. Reed and G. Ehrlich, J. Vac. Sci. Technol., In press.

4. W. R. Graham and G. Ehrlich, Phys. Rev. Lett. 31, 1407 (1973).

5. W. R. Graham and G. Ehrlich, J. Phys. F. 4, L212 (1974).

6. T. Sakata and S. Nakamura, Surf. Sci. 51, 313 (1975).

7. D. A. Reed and G. Ehrlich, Philos. Mag. 32, 1095 (1975).

8. T. T. Tsong, Phys. Rev. B6, 417 (1972).

9. In the terminology of statistics, the motion of the COM is better described as a birth-death process.

10. G. Ehrlich, J. Chem. Phys. 44, 1050 (1966).

   W. Feller, SIAM J. Appl. Math. 14, 864 (1966).

   E. W. Montroll, in Energetics in Metallurgical Phenomena, edited by W. M. Mueller (Gordon and Breach, New York, 1967), Vol. III, p. 123.

11. S. Karlin, A First Course in Stochastic Processes (Academic Press, New York, 1966), Chap. 7.

12. This approach has been used in chemical kinetics by D. A. McQuarrie, C. J. Jachimowski, and M. E. Russell, J. Chem. Phys. 40, 2914 (1964).

13. The superscript z will be dropped whenever the probabilities $P_i^{(z)}$ become independent of starting position.

14. P. G. Guest, *Numerical Methods of Curve Fitting* (Cambridge University Press, Cambridge, 1961).

15. The criteria for local equilibrium are now more stringent than for dimers, however. It must be established that energetically different trimer configurations are in fact accessed.

16. Here we retain the convention of letting the symbols a_I, etc. represent the rate of change between specified types of trimers. Thus a_I denotes the rate at which p_0^A changes to p_1^A, and b_{III} the rate from p_1^B to p_2^A, even though there are two equivalent jumps possible for these processes, and only one for the change from p_1^A to p_2^A.

17. Equation (86) provides a check on the self-consistency of the jump rates. Inasmuch as the system is in local equilibrium, $P_2^A = P_1^A$, and it follows from Eqs. (84) and (86) that the rates must satisfy the product rule

$$a_I b_{II} c_{III} = a_{II} b_{III} c_I$$

This is quite a general relation, and can be derived independently from transition-state theory.

FIGURE CAPTIONS

Fig. 1. Dimer configurations in one-dimensional diffusion. Shading denotes atoms forming diffusion channels, crosses denote the location of the center of mass for dimers. Direction of diffusion is indicated by arrows, surface spacing in this direction by ℓ.

Fig. 2. Random walk representation of dimer diffusion, showing a sequence of dimer configurations for COM positions x. Unit cell for the representative random walk is indicated by heavy lines. λ_x indicates rate constants for COM transitions to the right, and μ_x to the left.

Fig. 3. Representation of trimer diffusion. One particular, symmetrical sequence of configurations involved in the diffusion is shown at the top, together with the type of site. The unit cell, and the COM rate constants λ_x and μ_x to represent diffusion occurring via this sequence, are given below.

Fig. 4. Relative error in b/c as a function of the mean square displacement. All values for 100 observations, a diffusion interval t of 100 sec, $v_a = 5 \times 10^9 \text{ sec}^{-1}$, $v_b = v_c = 10^{10} \text{ sec}^{-1}$.

c > b > a: $E_a^{\ddagger} = 15$ kcal/mole, $E_b^{\ddagger} = 14$, $E_c^{\ddagger} = 13$

b > c > a: 15   13   14

a > b > c: 13   14   15

a > c > b: 13   15   14.

$P_1 = [2 + \exp(E_a^{\ddagger} - E_c^{\ddagger})/kT]^{-1}$.

Fig. 5.   Atomic configurations and rate constants for one-dimensional

motion of trimers. COM sites indicated by numerals. A and B

distinguish the two energetically nonequivalent configurations

possible at each site.