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TITLE: **CLASSICALLY EXACT SURFACE DIFFUSION CONSTANTS AT ARBITRARY TEMPERATURE**

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Classically Exact Surface Diffusion Constants at Arbitrary Temperature

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ABSTRACT

An expression is presented for computing the classical diffusion constant of a point defect (e.g. an adatom) in an infinite lattice of binding sites at arbitrary temperature. The transition state theory diffusion constant is simply multiplied by a dynamical correction factor that is computed from short-time classical trajectories initiated at the site boundaries. The time scale limitations of direct molecular dynamics are thus avoided in the low and middle temperature regimes. The expression results from taking the time derivative of the particle mean square displacement in the lattice-discretized coordinate system. Applications are presented for surface diffusion on fcc(100) and fcc(111) Lennard-Jones crystal faces.

I. Introduction

Molecular dynamics (MD) simulations have played an important role in the understanding of surface diffusion processes[1]. Single adatom diffusion constants can be computed by simply integrating the classical trajectory of an atom adsorbed on the desired crystal face, where the crystal is modeled by a finite cluster of atoms with periodic boundary conditions in the two directions parallel to the surface. The adatom diffusion constant (D) is then extracted from either the time derivative of the mean square displacement or from the time integral of the velocity autocorrelation function. Because surface diffusion is an activated process, this approach is limited to temperatures high enough, relative to the diffusion activation barrier, that the time between adatom diffusive jumps is short compared to the computer simulation time. Toller et al[2] have approached the diffusion problem by examining in detail the phase space properties of the saddle surface representing the barrier between two binding sites. In this way, they derive an expression for the true crossing rate of a diffusing particle, correcting for dynamically correlated recrossings of the barrier. However, no account is taken of multiple jumps that lead the particle to thermalize in a distant binding site. This type of event can be important, as will be seen below. At low temperatures, a different method can be employed[3], that exploits the rare event nature of the diffusion process. In this approach, D is first approximated by transition state theory[4](TST). That is, the rate constant for escape from a surface binding site is taken as the average rate at which site to-site crossings occur, and these crossings are assumed to be directionally uncorrelated. This TST diffusion constant (D^{TST}) can be computed using equilibrium methods rather than trajectories. The classically exact diffusion constant can then be obtained by correcting D^{TST} for correlated dynamical events (e.g., quick sequential jumps in the same direction by an activated adatom) using short-time trajectories that are initiated at the TST boundaries dividing the binding sites. The dynamical corrections formalism for correcting TST rate constants, whether for a two-state system[5] or for a many-state system[3], is valid only in the low temperature regime, in which correlated dynamical events occur on a much shorter time scale than the reactive events. With these two methods available for computing D at high temperature and low temperature, a difficulty arises in the intermediate temperature regime. Here direct MD is unfeasible and the dynamical corrections formalism is invalid.

A solution to this problem has been developed recently[6,7]. Although dynamical corrections to TST *rate constants* are not valid except at low temperature[3], it can be shown that dynamical corrections to *diffusion constants* are in fact valid at any temperature for which the lattice of binding sites is well defined[7]. The purpose of this paper is to present a brief overview of this method and its application to surface diffusion. In Section II, we summarize the derivation of the method. In Section III, we demonstrate its application to surface diffusion by calculating D for adatom diffusion on the fcc(100) and fcc(111) surfaces. These results are presented in more detail elsewhere[7,8].

II. Theory

The high-temperature dynamical corrections derivation has been presented in two different ways[6,7]. Starting from the low temperature dynamical corrections formalism[3,5], which gives the rate constants for transition between any two lattice binding sites (connected or not), it can be shown that the particular linear combination of these rate constants comprising the diffusion constant is valid at high temperature[7]. This results from a phase cancellation of the time-dependent part of the expression for D. Here we review the more direct approach[6], in which an expression is derived directly from the mean square displacement of a tagged, diffusing particle.

We take as our system a particle diffusing in an infinite lattice of binding sites. Because these sites cover the physical space of positions available to the diffusing particle, a discretized coordinate for the diffusing particle can be defined by

$$\mathbf{R}^d(t) = \sum_j^{\infty} \theta_j(t)\, \mathbf{R}_j \quad , \tag{1}$$

where

$$\theta_j(t) = \theta\, \{F_j[\mathbf{R}(t)]\} \quad . \tag{2}$$

Here $\theta\{\ \}$ is the standard step function, $\mathbf{R}(t)$ is the configuration-space coordinate of the particle at time t, $\mathbf{R}_j$ is the average position for the particle in state j, and $F_j(\mathbf{R})$ is a continuous, differentiable function with the property that

$$F_j(\mathbf{R}) \begin{cases} > & 0 \text{ if } \mathbf{R} \text{ is in state } j \\ = & 0 \text{ if } \mathbf{R} \text{ is on the boundary to state } j \\ < & 0 \text{ if } \mathbf{R} \text{ is outside of state } j \quad . \end{cases} \tag{3}$$

Thus, $\mathbf{R}^d(t)$ takes on the value of the average position of the state in which the particle resides at time t. The time derivative of the discretized coordinate for a particle passing from state i to adjacent state j is given by

$$\frac{d\, \mathbf{R}^d(t)}{dt} = v_i(t)\ \delta_i(t)\ [\mathbf{R}_j - \mathbf{R}_i] \quad , \tag{4}$$

where $v_i(t)$ is the velocity component normal to the boundary at $\mathbf{R}(t)$,

$$v_i = -\frac{\nabla F_i \cdot \mathbf{v}}{|\nabla F_i|} \tag{5}$$

(v_i is positive if the particle is exiting state i), and $\delta_i(t)$ is nonzero only at the boundary to state i,

$$\delta_i(t) = \delta\,\{F_i[\mathbf{R}(t)]\}\ \ |\nabla F_i[\mathbf{R}(t)]| \tag{6}$$

($\delta\{\ \}$ is the Dirac delta function). This convention matches that used previously[3].

The derivation proceeds as follows. The diffusion constant can be written as

$$D = \frac{1}{2\alpha}\ \frac{d}{dt_0}\ \langle|\mathbf{R}(t) - \mathbf{R}(t_0)|^2\rangle\ , \tag{7}$$

where α is the dimensionality of the space and $t - t_0$ is assumed to be longer than the memory time of the diffusing particle. The brackets $\langle ... \rangle$ indicate the usual canonical ensemble average. [An average over a weighting function (w) other than $e^{-\beta H}$ will be indicated by a right-hand subscript. One restricted to the configuration space of state i will be written $\langle P\rangle_i$, where $w_i = \theta_i(0)\ e^{-\beta H}$]. Performing the time derivative in Eq. (7) over discretized coordinates (setting $t_0 = 0$) leads to

$$D = \frac{1}{2\alpha}\ \langle 2\left[\frac{d\mathbf{R}}{dt}\right]_{t=0}\cdot\ [\mathbf{R}(t) - \mathbf{R}(0)]\rangle$$

$$= \frac{1}{\alpha}\sum_i \chi_i \sum_j \langle \eta_j^{\pm}(0)\delta_i(0)\ v_i(0)\ [\mathbf{R}_j - \mathbf{R}_i]\cdot[\mathbf{R}^d(t) - \overline{\mathbf{R}}_{ij}]\rangle\ . \tag{9}$$

Here χ_i is the mole fraction for state i

$$\chi_i = \langle\theta_i(t)\rangle\ , \tag{10}$$

$\theta_j^{\pm}(0)$ is defined by $\theta_j^{\pm}(0) = \theta_j(0+) + \theta_j(0-)$, and $\overline{\mathbf{R}}_{ij} = \frac{1}{2}(\mathbf{R}_i + \mathbf{R}_j)$. The sum over j picks out all the states adjacent to state i, and $\theta_j^{\pm}(0)$, in conjunction with $\delta_i(0)$, picks out only those trajectories that are poised at the i-j boundary at $t = 0$.

Equation (9) gives the diffusion constant in terms of trajectories that are at the TST boundaries at $t = 0$, thus overcoming the rare-event problem at low temperatures. Moreover, as long as these trajectories are run long enough that the particle memory is lost, the expression is valid at any temperature for which the lattice of binding sites is well defined. We now manipulate Eq. (9) to arrive at a more computationally convenient form.

The TST rate of escape from state i is given by[3,5]

$$k_{i\to}^{TST} = \frac{\langle\, |v_i(0)|\, \delta_i(0)\,\rangle}{2\chi_i} \quad . \tag{11}$$

Defining the weighting function for a Maxwellian flux of particles through the TST border to state i,

$$w_{MF_i} = \theta_i(0)\delta_i(0)|v_i(0)|\, e^{-\beta H} \quad , \tag{12}$$

$k_{i\to}^{TST}$ can be written as

$$k_{i\to}^{TST} = \frac{\int w_{MF_i}\, d\mathbf{R}\, d\mathbf{p}}{\int w_i\, d\mathbf{R}\, d\mathbf{p}} \quad . \tag{13}$$

Substitution of Eq. (13) into Eq. (9) yields

$$D = \frac{1}{a} \sum_i \chi_i\, k_{i\to}^{TST} \sum_j \langle \theta_j^{\pm}(0) \frac{v_i(0)}{|v_i(0)|}\, [\mathbf{R}_j - \mathbf{R}_i] \cdot [\mathbf{R}^d(t) - \overline{\mathbf{R}}_{ij}] \rangle_{MF_i} \quad . \tag{14}$$

By symmetry, the summation over i need only span the basis states of the periodic infinite system. The integration over all space, e.g., in the definition of χ_i in Eq. (10), should be similarly restricted to this subspace of representative states. Once the TST boundaries have been specified, the evaluation of Eq. (14) involves computing $k_{i\rightarrow}^{TST}$ for each unique state, e.g., using configuration-space Monte Carlo[9], and integrating MD trajectories that are initiated at each unique TST boundary. The trajectory initial conditions can be obtained by sampling from a configuration-space Metropolis walk[10] restricted to the TST boundary. For the diffusing particle, the initial momentum along the direction normal to the TST boundary is chosen randomly from a Maxwellian-flux distribution, as dictated by the weighting function in Eq. (12). The momenta for other the coordinates in the system, including the two perpendicular coordinates of the diffusing particle, are randomly selected from a standard Maxwell distribution. These trajectories are then integrated long enough that the memory of the initial conditions are lost, after which time D from Eq. (14) maintains a plateau value with statistical fluctuations, as shown below.

III. Lennard-Jones Surface Diffusion

The method outlined above is now applied to the problem of adatom self-diffusion on the Lennard-Jones fcc(100) and fcc(111) surfaces. The calculations summarized in this section are described in detail elsewhere[7,8]. To perform MD to high accuracy, the Lennard-Jones potential is cut off smoothly using a spline between $r = 1.5\sigma$ and $r = 2.5\sigma$[11]. Each surface is modeled using a finite cluster of atoms with periodic boundary conditions parallel to the face, with the system size governed by the 2.5σ cutoff distance. In both the TST and MD simulations, the atoms in the top layer of substrate are free to move while deeper layers were held fixed. The binding site definitions [see Eq. (3)] are dependent only on the adatom coordinates, with the substrate top layer, equilibrium positions defining the vertices for a square lattice of binding sites on fcc(100) and a triangular lattice on fcc(111), as shown in Fig. 1. For the (100) surface, there is only one unique binding site. However, the (111) surface has two types of binding sites, corresponding to the fcc and hcp positions for seeding the next substrate layer. Thus the evaluation of the diffusion constant for the (111) surface requires two sets of trajectories: one initially entering an fcc site and the other initially entering an hcp site.

Figure 2 shows the results for fcc(100) at T=0.345 (all temperatures and times are in Lennard-Jones reduced units). This temperature, roughly half the melting point, was chosen to illustrate that Eq. (14) can be successfully applied even at temperatures in the direct MD regime. At lower temperatures, the method is even more easily applied because a smaller number of uncorrelated jumps would be expected to occur on the time scale of the dynamically correlated events. This, in turn, leads to better statistics. The evaluation of Eq. (14) at t=0 yields the TST diffusion constant. In the case of one unique binding site,

$$D^{TST} = \frac{1}{2\alpha} k_{i\rightarrow}^{TST} l^2 \quad , \tag{15}$$

where α is the space dimensionality and l is the distance between adjacent binding sites. Using the Monte Carlo method mentioned above, $k_{i\rightarrow}^{TST}$ is computed to be $0.10 \pm .01$. From this we obtain $D(t = 0+) = D^{TST} = 0.035 \pm .006$, as shown in Fig. 2. Values at positive times were computed by means of Eq. (14) with a set of 1948 trajectories. The correlated dynamical events have ended by approximately $t = 14$, which is comparable to the average time between adatom jumps at this temperature $[(k_{i\rightarrow}^{TST})^{-1} = 10.1 \pm 0.4]$. For comparison, the value of D computed from direct MD (0.038 ± 0.004) is indicated on Fig. 2. This was computed from Eq. (7) using trajectories that were integrated for the same length of time as the saddle point trajectories, but whose initial conditions were not confined to the TST boundary. The two methods for computing D are seen to agree.

Figure 3 shows the temperature dependence of the dynamical correction factor, D/D^{TST}. At very low temperatures, $D/D^{TST} = 1$, because the adatom crossing the saddle point has virtually no excess energy; subsequent interactions with substrate atoms, which on average will lower its energy, leave it with too little momentum to cross another boundary. It should be noted that if a position other than the symmetric saddle point were chosen for the TST boundary, D/D^{TST} would be less than unity at $T = 0$. [However, Eq. (14) would still be valid.] At high temperatures, D/D^{TST} increases with T. This arises from the increase in excess energy of the adatom, which gives a greater number of correlated events in the form of directionally aligned multiple jumps along a given direction. This has been previously observed in analyses of direct MD trajectories[12-14] for both the surfaces studied here. The effect is more pronounced on the (111) surface because the diffusion activation barrier ($E_A \approx 0.30$) is much lower than for the (100) surface ($E_A \approx 1.55$).

An effect that has not been previously observed is that D/D^{TST} dips below unity for fcc(111), with a minimum at about $T = 0.04$. This results from the fact that at low temperatures, with the substrate atoms near their equilibrium positions, an adatom has a reasonable probability of entering the binding site nearly perpendicular to the two-atom TST "gate," bouncing off the substrate atom at the far side of the binding site, and retracing its path back through the same TST gate. Inspection of Eq. (14) shows that this contributes negatively to D. In contrast, the type of double jump that increases

D/D^{TST}requires that the adatom change direction by 60°, while maintaining enough energy to clear the next saddle point. This type of event does not dominate until above T=0.1.

IV. Conclusions

We have demonstrated that rigorous, classical surface diffusion constants can be computed at arbitrary temperature using transition state theory augmented by short-time classical trajectories. This method, which can also be applied to solid state diffusion, thus represents a unified approach to computing point defect diffusion constants. In the fcc(111) and fcc(100) examples presented here, the dynamical correction factor, D/D^{TST}, increases with T at high temperatures, as expected from considerations of the energy of the adatom relative to the diffusion barrier. On the (111) surface, D/D^{TST}shows an interesting dip below unity at low temperature, caused by concerted bounce-back recrossings.

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Figure Captions

FIG. 1. Top layer of the substrate clusters used to compute diffusion constants for the Lennard Jones system. (a) fcc(100); (b) fcc(111), with hcp sites indicated by small circles. The TST boundaries for the unique binding sites are shown.

FIG. 2. Diffusion constant (in reduced units) for Lennard-Jones fcc(100). D(t) from Eq. (14) is plotted with error bars representing a 90% confidence interval. The solid line at $D = 0.038$ is the direct MD result, with associated error limits indicated by dashed lines. For the saddle point trajectories, the circles give the number of new diffusive jumps, relative to the total number of trajectories (1948), per $\Delta t = 1.56$ time interval. Correlated events are seen to end by approximately $t = 14$.

FIG. 3. Temperature dependence of the dynamical correction factor for adatom diffusion on fcc(100) (squares) and fcc(111) (triangles).

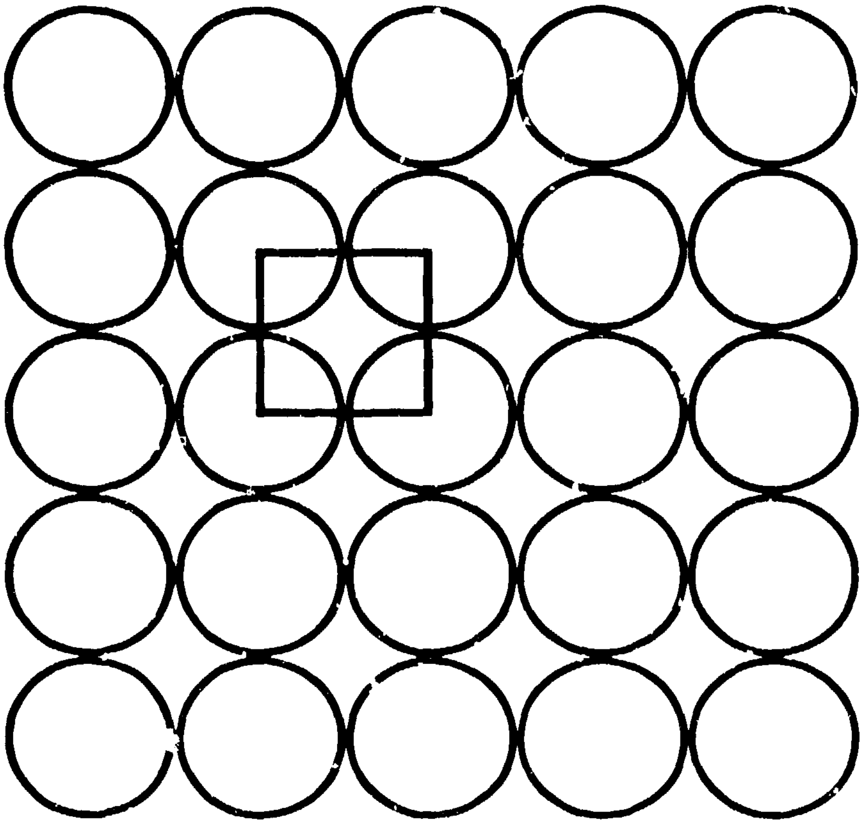

Fig 1a

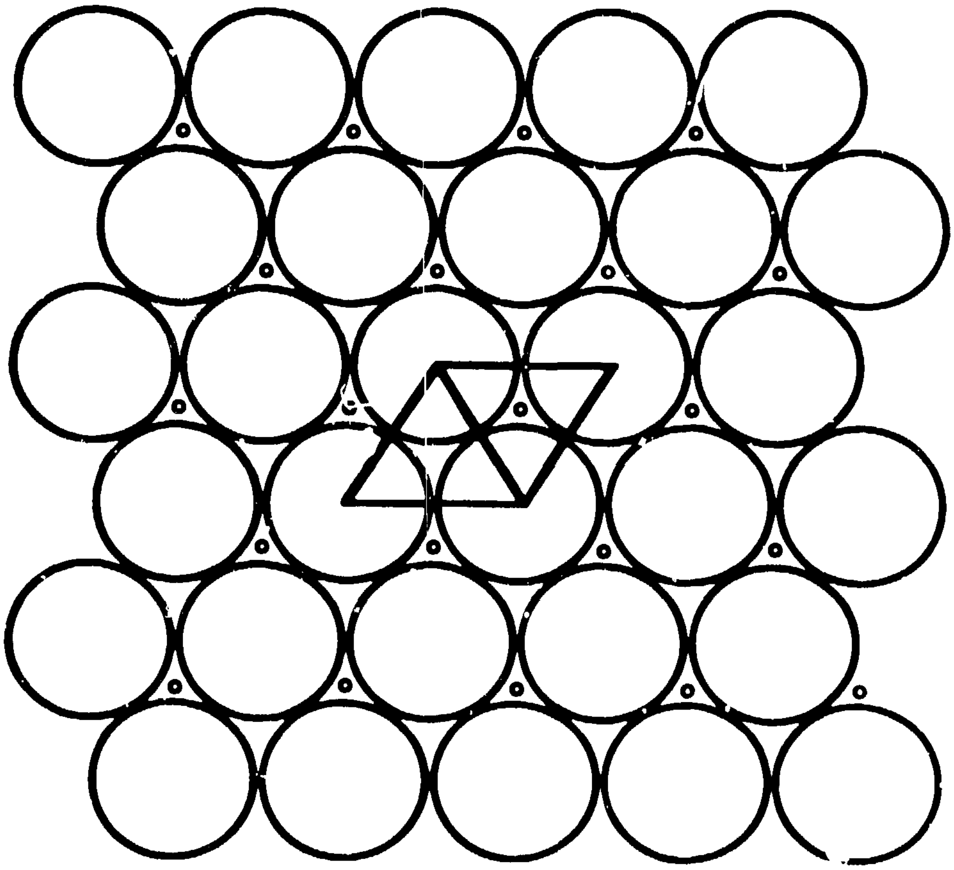

Fig 1b

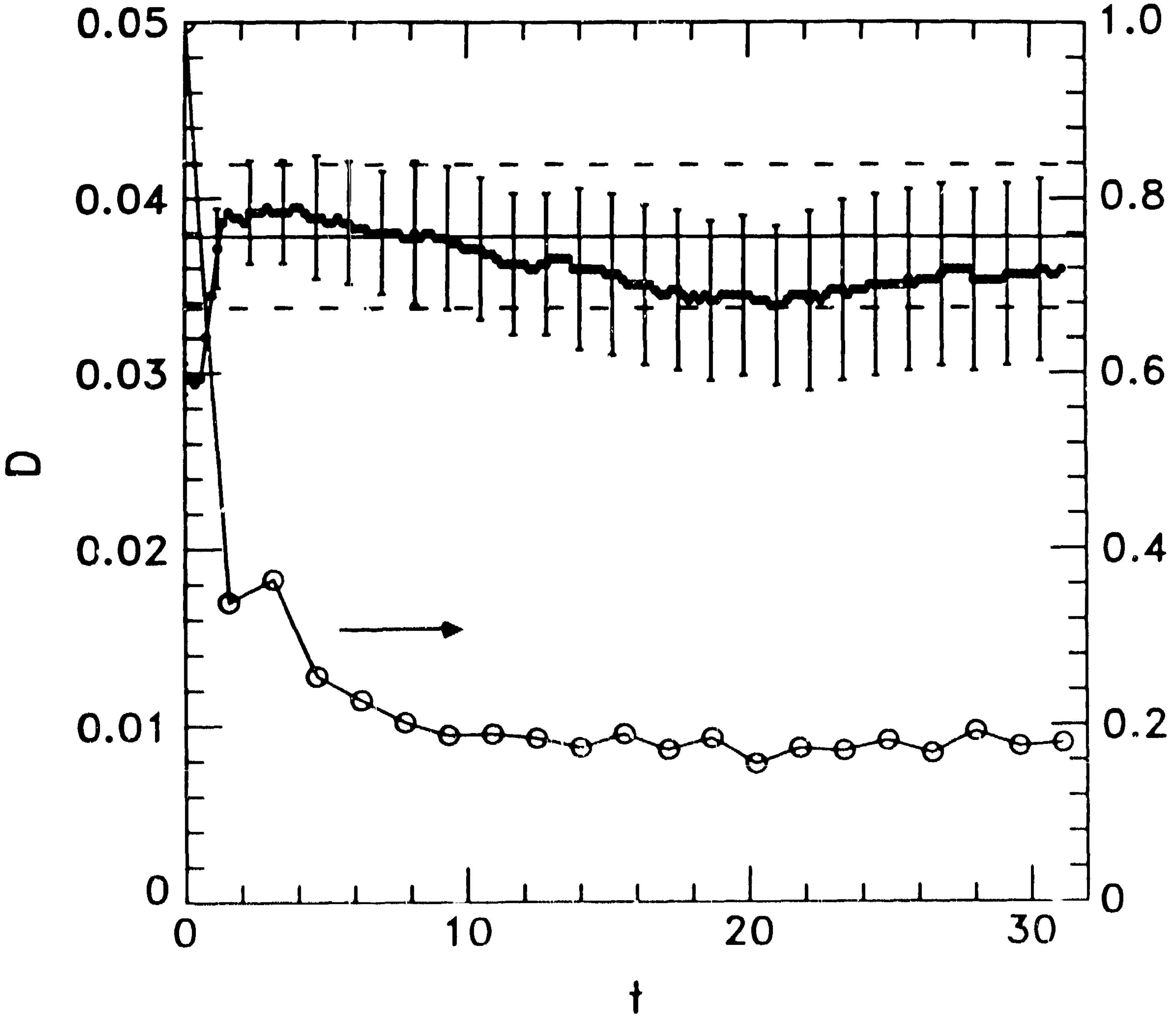

Fig 8

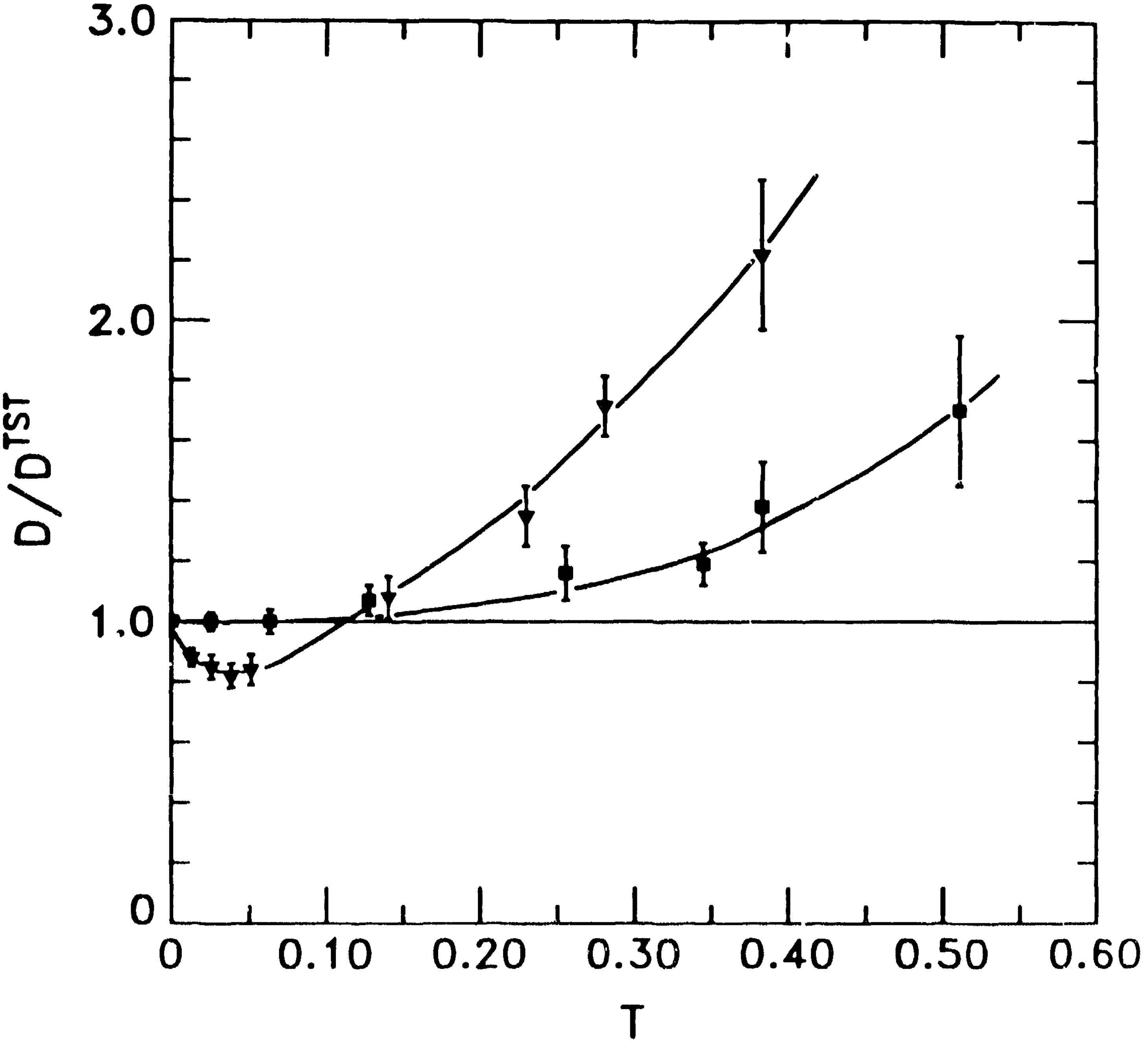

Fig 3