JOURNAL OF MATERIALS SCIENCE 27 (1992) 3125–3132

Review

The path probability method: an atomistic technique of diffusion

SHEIKH A. AKBAR
Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210, USA

The path probability method (PPM) of irreversible statistical mechanics has been successfully applied to various diffusion problems. The major advantage of this atomistic treatment over the phenomenological approach of irreversible thermodynamics is that all Onsager matrix coefficients can be derived analytically so that relations among measurable quantities can be clearly understood in terms of microscopic parameters. This review article attempts to present the PPM in the simplest possible form. The importance of the PPM as an atomistic technique is illustrated using a simple example. The applicability and limitations of the technique are also emphasized.

1. Introduction

Atomic transport (diffusion) plays an important role during the processing and use of materials at high temperatures. In many cases, this is the single most important process occurring. For instance, atomic transport often provides the means by which the solid is fabricated (e.g. sintering, interdiffusion, etc.). Atomic transport is sometimes the phenomenon which is utilized in devices, e.g. sensors utilizing solid electrolytes. This phenomenon can also be responsible for the limited lifetime of materials in service, e.g. creep, oxidation, demixing, etc.

Diffusion in solids is a well established area of research, and it appears that the fundamental concepts of diffusion have been well accepted. However, the treatment of diffusion has mostly been phenomenological in nature, and fails to provide much understanding at the microscopic level. Although in simple cases, a formal solution of Fick's equation can give satisfactory answers, in most cases it is difficult to find correct interpretations based on a phenomenological treatment. Even if one resorts to the Onsager equations of irreversible thermodynamics, it is often difficult to define clearly driving forces for diffusion and to derive the content of the Onsager matrix well enough to achieve a clear understanding.

Atomistic treatments based on random-walk theory have been quite successful in deriving the correlation factor in tracer diffusion [1–3]. In this case, because single elements are treated in the limit of very low defect concentration, no complicated model is required and diffusion can be calculated in a straightforward fashion. Nonetheless, the contribution of this atomistic approach to our understanding of diffusion has been quite significant. It is clear, therefore, that an atomistic theory to treat diffusion in more complex cases such as highly defective solids and multicomponent interacting systems is likely to lead to a clearer understanding.

The essence of an atomistic theory of diffusion is to derive the Onsager equation in a multicomponent system

$$J_i = -\sum_j L_{ij} X_j \qquad (1)$$

where J_i and X_i represent, respectively, the flow and the driving force for diffusion of the ith species, and L_{ij} is the Onsager matrix coefficient. Such analytical expressions are quite helpful in identifying measurable quantities (e.g. diffusion coefficient, ionic conductivity, etc.) in terms of atomistic parameters such as jump frequencies and interatomic interactions. If sufficient information is available on these quantities, specific predictions can be made or, conversely, diffusion experiments can be used to evaluate these fundamental properties for which there is no straightforward method of calculation or measurement.

The path probability method (PPM) of irreversible statistical mechanics has been quite successful in deriving the Onsager equation analytically based on microscopic models. The major advantage of this technique is that all Onsager matrix elements and, hence, measurable transport properties can be identified in terms of microscopic variables. This is not an alternative technique, but rather serves as a supplement to the well established atomistic treatments of simple cases, the phenomenological treatment of multicomponent diffusion, the linear response theory and computer simulations.

Although the PPM has proven to be versatile, there is a lack of clear understanding of the nature of approximations in the technique. In this context, it is especially important to recognize where the PPM stands in relation to other atomic theories of diffusion such as the pair-association method [4], the master equation method [5], and the Monte-Carlo simulation method [6]. This will be discussed later, once the principles of the technique have been introduced.

2. Formalism of the PPM

The original paper by Kikuchi [7] gives an excellent introduction to the PPM, and a review article by Sato [8] explains its basic principles and applicability to transport problems. Here, only the characteristic features of the technique will be reviewed very briefly.

The path probability method is an extension of the cluster variation method [9] (CVM; also developed by Kikuchi) of equilibrium statistical mechanics to time-dependent processes. The extension is easy to follow once the technique of the CVM is understood.

The CVM can be characterized as a technique based on the variation principle common to equilibrium statistical mechanics. In essence, the equilibrium state is represented by the most probable state specified by the state variables $\{a\}$ which make the free energy $F\{a\} = E\{a\} - TS\{a\}$, a minimum, or the partition function $Q\{a\} = \exp[-F\{a\}/kT]$, a maximum. The choice of the state variables $\{a\}$ which represent energy $E\{a\}$, and the evaluation of entropy $S\{a\}$ are the basic ingredients of the CVM.

For example, if atoms interact only as nearest neighbours in a crystalline lattice system, the total energy $E\{a\}$ of the system can be given by specifying the number of atomic pairs of each kind. The entropy $S\{a\}$ can be evaluated by counting the number of ways of rearranging these fixed number of pairs on the lattice points (details can be found in [9]). When these pairs are taken as state variables, the treatment is called the pair approximation.

In its general form, the CVM represents a hierarchy of approximations. Depending on the size of a basic cluster, they are successively called the point (Bragg–Williams), pair (Bethe), triangle, tetrahedron, octahedron approximations, etc. The degree of approximation in the CVM can be improved systematically by increasing the size of the basic cluster.

The PPM deals with the time evolution of the state. These states, specified at a time instant, are described by the state variables as used in the CVM. A change of the state occurs via a unit process. This unit process, in the case of diffusion, is a jump of an atom to its neighbouring vacant site. This process, therefore, connects a pair of lattice sites. The probability that a particular process occurs can be utilized as a variable to characterize a change of a state. These are called the path variables. In the PPM, a set of path variables $\{A\}$ is defined and the path probability function (PPF), $P\{A\}$, is constructed in a corresponding fashion to constructing the partition function in the CVM. The PPF is conveniently divided into three factors [10]. The first one corresponds to the transition probability of the system for which there is no counter part in the free energy function (FEF) of the CVM. The second factor is a generalization of the energy factor in the CVM, and consists of terms such as activation energy of jumps and energy required to break bonds with neighbouring atoms. The third one corresponds to the entropy factor, and is calculated by counting all possible ways of constructing the paths. The most probable paths (or changes) are then determined by maximizing $P\{A\}$. The correspondence between the PPM and its equilibrium counterpart, the CVM can be summarized as shown in Table I. This correspondence makes the PPM very tractable at the microscopic level.

The minimization of the free energy (or maximization of entropy) in the CVM is to find the state of "largest probability" of appearance. This procedure is based on the theory of probability concept, and is more fundamental than the second law of thermodynamics [11]. In fact, the second law is derived from it. However, this procedure is based on a basic postulate that each state being considered has the equal *a priori* probability of appearance. Kikuchi used the concept of the largest probability in the PPM as well. The path which is observed is the path of most probable occurrence. This is not derived from the second law, but holds when the basic postulate holds. The postulate is that every path being considered is *a priori* equally probable, or appears with a certain probability. This maximization holds, however far the state may be away from equilibrium. Usually Markovian processes are treated in the PPM, but according to Kikuchi, a similar path concept can be used in non-Markovian cases. Moreover, the PPM is not limited to the most probable path only, but fluctuated paths away from most probable ones are also contained in the formalism [10].

A consequence of the maximization process in the PPM is that the distribution in the overall transition probability is given as an average of the state and not as the instantaneous value when the atom is about to jump. Accordingly, the PPM has not been very effective in treating transport problems where the motion of individual particles is at stake (e.g. the calculation of the correlation factor). In fact, as will be discussed later, any technique using statistical mechanics should have this problem as an inherent element. Sato [12, 13] has determined a way to correct this problem within the pair approximation by changing some of the averaging processes of the original PPM.

It has been established that in the pair approximation of the PPM, the most probable path expressions can be written simply by inspection without going through detailed calculations [7, 8]. For example, the expression for the most probable path for an

TABLE I

CVM	PPM
Define state variables	Define path variables
Construct free energy function (FEF)	Construct path probability function (PPF)
Minimize FEF	Maximize PPF

atom exchanging with a vacancy to the right can be written as

$$Y_{+i}^{(n)} = w_i \Delta t\, y_{iv}^{(n)} \left[\frac{\sum_j y_{ij}^{(n)} K_{ij}}{x_i^{(v)}} \right]^{\omega - 1} \left[\frac{\sum_j y_{ji}^{(n-1)} K_{ji}}{x_i^{(v)}} \right]^{\omega} \quad (2)$$

where

$$w_i = \theta_i \mathrm{e}^{-\beta u_i}$$

$$\beta = 1/kT$$

and

$$K_{ij} = \mathrm{e}^{-\beta \varepsilon_{ij}}$$

Here, θ_i represents the attempt frequency, u_i is the reference activation energy (in the absence of the interactions), 2ω is the co-ordination number of the lattice, Δt is the time interval during which an atomic jump occurs, ε_{ij} is the interatomic interaction, $x_i^{(v)}$ is the atomic fraction on the vth atomic plane, and $y_{ij}^{(n)}$ is the probability of finding a pair i–j across the nth bond (Fig. 1). The subscript v is used to denote vacancy and, hence, y_{iv} represents the probability of finding a vacancy near an atom i. This term is conveniently called the vacancy availability factor. The bracketed terms represent the effect of the surrounding on the jumping atom and is called the bond-breaking factor. A physical image of the bond-breaking factor is shown in Fig. 1 for a b c c lattice ($2\omega = 8$). Notice that across the nth bond, $(\omega - 1)$ bonds need to be broken, because one of the neighbouring sites is a vacancy. Equation 2 tells us precisely how the jump of an atom depends on the availability of vacancy in its neighbourhood, and how the jump is influenced by the surrounding atoms. Similarly, an expression can be written for path variable involving exchange to the left, $Y_{-i}^{(n)}$. The generalization of the inspection scheme for higher than the pair approximation is not straightforward and, yet to be formulated.

The atomic flow is then defined across a lattice plane in terms of the net change of number of atoms in a particular direction (this is proportional to the difference in the path variables associated with the atom–vacancy exchange in opposing directions, i.e. $Y_{+i}^{(n)} - Y_{-i}^{(n)}$). The Onsager equation for diffusion is finally derived by evaluating these path variables in the linear range. Such derivations have been illustrated step-by-step in earlier publications [7, 8, 14, 15].

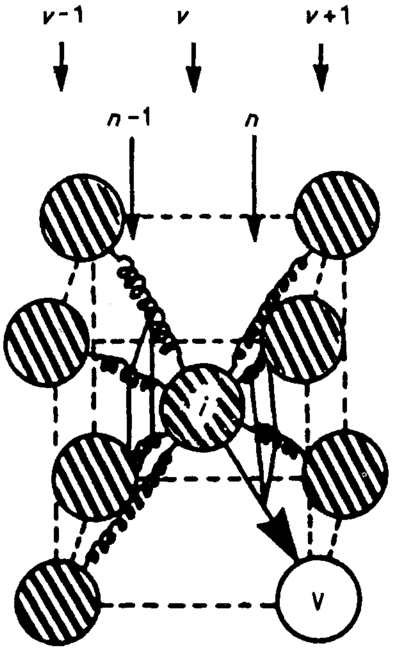

Figure 1 Effect of bond breaking as the ith atom on the vth atomic plane exchanges with a vacancy on the $(v + 1)$th plane across the nth bond. Springs indicate the bonds [8].

Like most treatments, the PPM in the past has also been restricted to linear-range calculations. Such calculations are very useful for characterizing transport processes in a material near equilibrium when imposed forces are small. In real-life applications, however, the driving force for atomic diffusion may be so large that the validity of the linear-range Onsager equation is not warranted, and it is important to include non-linear contributions. It should be noted that the PPM can easily be extended to include such contributions by keeping terms of higher order in the expansion of the path variables.

3. Flow expressions by the PPM

The importance of an atomistic treatment such as the PPM can be better illustrated by choosing an example. For the sake of simplicity, a one-component system exposed under a chemical potential gradient, $\dot{\mu}_1$, and a temperature gradient, $\dot{T}$, is chosen. In such a case, the atomic flow, J_1, and the heat flow, J_Q, derived by the PPM in the pair approximation can be expressed as

$$J_1 = -\left(\frac{L_{11}}{T}\right)\dot{\mu}_1 - \left(\frac{L_{1Q}}{T}\right)\dot{T} \quad (3a)$$

$$J_Q = J_1 Q_1 - K^* \dot{T} \quad (3b)$$

where

$$L_{11} = a^2 Y_1 \quad (4a)$$

$$L_{1Q} = Q_1 L_{11} \quad (4b)$$

$$K^* = L_{11}[E_1^2 - 2\mu_1 E_1 + \mu_1^2 - (2\omega - 1)\Delta\varepsilon^2/2] \quad (4c)$$

where a is the jump distance, and K^* is the thermal conductivity due to atomic transport. The energy of transport, E_1, the heat of transport Q_1, and the jump probability, Y_1, are expressed as

$$E_1 = u_1 + \varepsilon_1^* \quad (5a)$$

$$Q_1 = E_1 - \mu_1 \quad (5b)$$

$$Y_1 = \Delta t \hat{W}_1 y_{1v} \quad (5c)$$

In the above expressions, ε_1^* represents the effective interaction (the word effective indicates that the quantity includes the effect of the neighbouring atoms). The term $\Delta\varepsilon$ represents the feedback effect which indicates the compensation of the effect on the reference system when a flow of a finite number of particles is measured [14]. The other terms are the same as introduced earlier. The effective jump frequency, $\hat{W}_1$, is expressed in terms of the bare exchange frequency, w_1, and the bond-breaking factor, F, as

$$\hat{W}_1 = w_1 F \quad (6)$$

with

$$W_1 = \theta_1 e^{-(u_1/kT)} \qquad (7a)$$

$$F = \left(\frac{y_{11} e^{-\varepsilon_{11}/kT} + y_{1v}}{x_1} \right)^{(2\omega - 1)} \qquad (7b)$$

Again, notice that the jump probability consists of the vacancy availability factor, y_{1v}, and the bond-breaking factor. In the case of an ideal solution ($\varepsilon_{ij} = 0$), F would be unity indicating that the surrounding atoms would not have any effect on the jumping atom. A major consequence of the PPM derivation of thermal diffusion is that the content of such quantities as the energy of transport, E_1, and the heat of transport, Q_1, can be identified in terms of microscopic quantities, which has not otherwise been possible. This example clearly shows how a transport problem can be described in terms of detailed atomistic features by applying the PPM. In a multicomponent system, similar microscopic features appear in an integrated fashion [14, 16–18].

4. Applicability and limitations of the PPM

The PPM has been applied to a variety of transport problems such as thermal diffusion [14, 16–19], chemical diffusion in multicomponent alloy systems [20], superionic conduction [21–31], tracer diffusion [8, 13, 32–36], demixing of oxides [15–17, 37, 38], the mixed alkali effect [39–41], oxygen diffusion in high T_c superconductors [42], kinetics of phase transformation [43–46], evolution of cellular structure [47] and kinetics of crystal growth [48–50]. Instead of discussing all of the applications, a few will be highlighted to illustrate the significance of the PPM as a microscopic technique.

During the past few years, an atomistic approach for treating the demixing problems in multicomponent oxides has been developed based on the PPM. The demixing, defined as a change in the composition of a multicomponent system created due to the difference in the diffusivities of the constituent components, can be a significant source of deterioration of materials in high-temperature technologies [38, 51–55]. The PPM treatment enables one to correlate demixing behaviour to microscopic material properties and, thus, serves as a complement to the phenomenological treatments. In addition to confirming most of the results of the phenomenological treatments, the atomistic approach has been able to give some new insights into the problem.

The atomistic treatment, for the first time, was able to clearly identify the difference between the Soret effect and the demixing effect [16]. Some demixing experiments have been carried out for binary oxides under a temperature gradient under a variety of boundary conditions [52]. Among these, experiments performed in the presence of an oxygen atmosphere in contact with the specimen can allow the flow of vacancies in and out, and this is called the open case [38]. This corresponds to the demixing effect. In the experiments under a temperature gradient on encapsulated samples, on the other hand, specimens are not in contact with an oxygen environment and do not allow the flow of vacancies. This case is called the closed case and corresponds to the Soret effect.

The application of the PPM to this problem revealed some new physics. In the closed case, the concentration of vacancies plays an important role in the redistribution of the constituents [18, 19]. If the vacancy concentration is low, it is difficult to pack more particles into the lattice (the compressibility is low) and the cations redistribute in the opposite directions (Fig. 2) in a way not to change the vacancy distribution. On the other hand, if the vacancy concentration is high, the redistribution can occur in the same direction (Fig. 3). In the open case, on the other hand, only the ratio of vacancy concentrations (determined by the P_{O_2}) on the two surfaces plays an important role in determining the demixing profile. The difference between the open case and the closed case is readily seen in Fig. 4. It is to be noted that in the open case (curve a), the effect is far greater than that in the closed case (curve b) which agrees with the experimental results [56]. The most important feature to notice, however, is that because of the difference in the compressibility in the two cases, the accumulation of the same species occurs in the reverse directions. Identification of such a difference in boundary conditions indicates the capability of the atomistic treatment.

The PPM was also applied to study the transient behaviour of the demixing [15]. One of the important conclusions of the work is that the time evolution of the demixing can essentially be represented by a diffusion equation (equivalent to Fick's second law) and, hence, the time required to reach the steady state is determined by the time needed for atoms to percolate

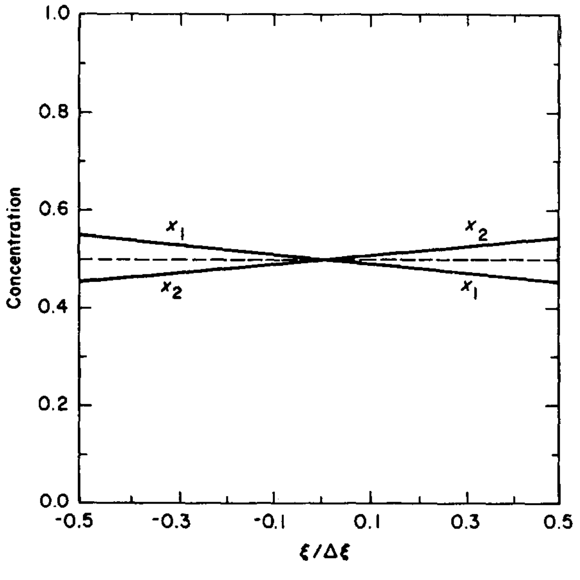

Figure 2 Two-component Soret effect for low vacancy concentration [18]. The abscissa represents the coordinate ξ normalized by the length of the sample $\Delta\xi$ along the diffusion direction. T_1, T_2, temperatures of the two surfaces ("left" surface is the low-temperature side); x_3, the vacancy concentration; x_1, x_2, concentration of the two components; u_1, u_2, activation energy of motion for components 1 and 2, respectively. $u_1 = 1.5$, $u_2 = 1.0$, $T_1 = 1200$, $T_2 = 1300$, $x_3 = 10^{-3}$.

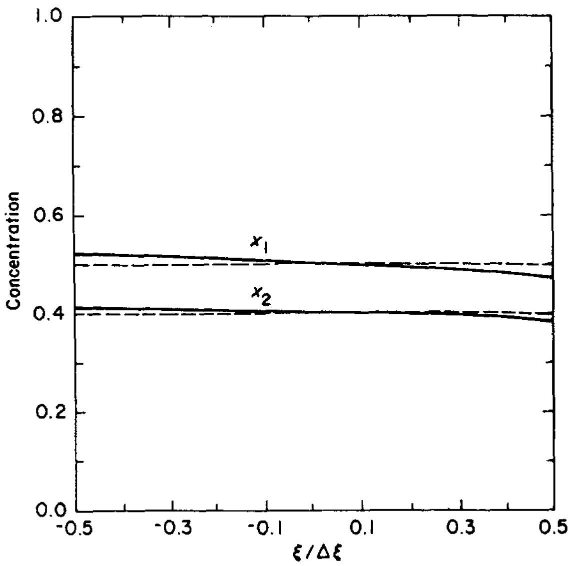

Figure 3 Two-component Soret effect for high vacancy concentration [18]. $u_1 = 1.05$, $u_2 = 1.0$, $T_1 = 1200$, $T_2 = 1300$, $x_3 = 10^{-1}$.

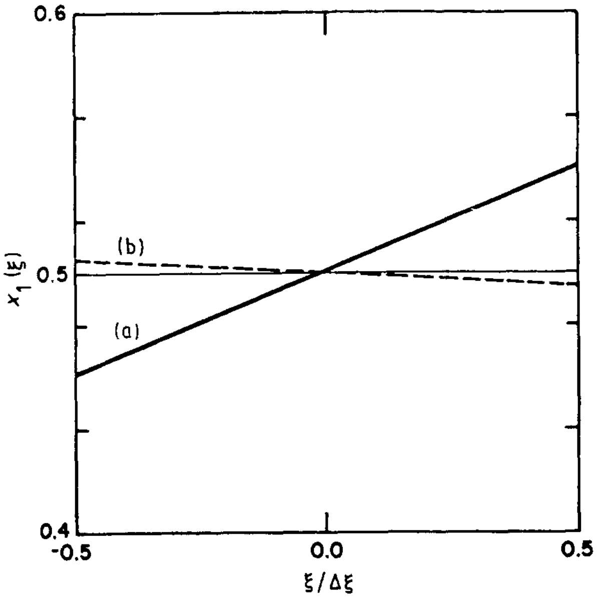

Figure 4 Comparison of the demixing behaviour in (a) the open case and (b) the closed case, calculated by the PPM using the same parameters [16].

through the entire length of the specimen. The treatment also substantiated the usually adopted assumption that the "local equilibrium condition" holds even for the non-steady state diffusion process provided that the change of macro variables, such as concentration, is slow compared with the frequency of a unit process (e.g. jump of an atom to a vacancy). However, this assumption is not valid during the very early stage of the transient behaviour, and poses serious limitations to the applicability of the PPM to the problem. Because the local equilibrium condition is implicitly used in deriving the transition probabilities in the PPM, the treatment of the early stage of a transient behaviour is yet outside the scope of the technique and remains as a challenging future problem.

The PPM has extensively been applied to transport problems in superionic conductors [21–31]. One of the common characteristic features of these materials is the existence of a large number of available sites which makes them highly defective. These are a group of solids, for example, which cannot be handled by any straightforward extension of the random-walk theory of diffusion. In fact, only the PPM and the Monte Carlo method have so far been successfully applied to treat transport problems in these materials.

The application of the PPM has mainly been to the transport problems in the two-dimensional honeycomb lattice of β-alumina superionic conductors. One of the important predictions of the calculation is the appearance of the "physical correlation factor, f_I," in the ionic conductivity [21]. This term has a strong compositional dependence as shown in Fig. 5, which has also been confirmed by the Monte Carlo calculation [57].

The existence of the physical correlation factor was not even suspected in the past [58, 59]. This factor arises because of the fact that the diffusion (conduction) path of ions in solid is strictly limited and the motion of ions often deviate from the random-walk. This factor represents the efficiency of the motion of the assembly of ions towards a long distance conduction and, hence, it is more appropriately called the "percolation efficiency". The percolation efficiency depends on the topology of the diffusion (conduction) path, and is measured relative to that of the random-walk. If the key sites of conduction paths are blocked for some reason, the percolation efficiency and hence the conductivity can drop drastically. On the other hand, local motion of ions is not seriously affected. In such a case, if the ionic conductivity is measured at high frequencies, the drop in the conductivity due to blocking is expected to vanish [60]. Based on the concept of the percolation efficiency, Sato *et al.*

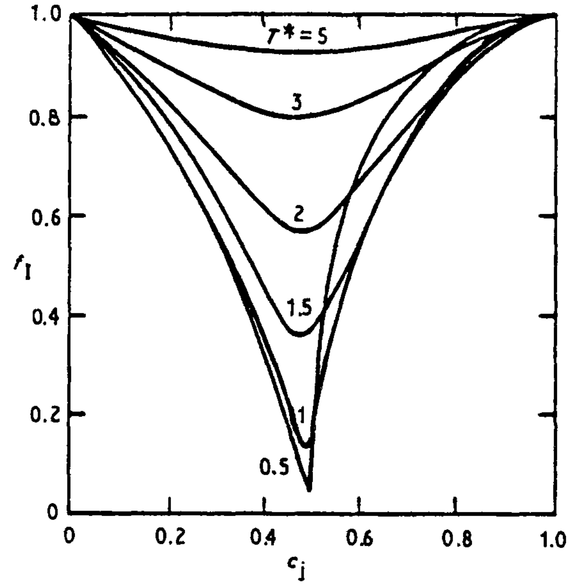

Figure 5 The composition dependence of the physical correlation factor, f_I, in the honeycomb lattice of β-alumina [21]. The reduced temperature is defined as $T^* = kT/|\varepsilon|$, where $|\varepsilon|$ is the magnitude of the interaction between the nearest neighbouring conduction ions. Notations c and x have been interchangeably used to denote composition in this paper.

[39–41] have been successful in explaining most features of the mixed alkali effect (MAE). The MAE, observed in glasses [61, 62] and β-aluminas [63–67], represents a drastic drop in the ionic conductivity producing a minimum in intermediate compositional range, as one type of alkali ion is progressively replaced by another type of alkali ion. This is believed to be due to the blocking of conduction paths by one kind of ion created by the mutual interactions among different kinds of ions [41]. A detailed review of the physical correlation factor can be found in [58].

Recently, the PPM has been applied to the problems of chemical diffusion in multicomponent alloys [20]. One of the outstanding problems in this area is to understand the thermodynamic features of diffusion paths such as the location of the zero-flux plane (ZFP) [68–70]. The distribution of compositions due to interdiffusion is represented by a curve which connects the compositions of terminal alloys in the composition diagram [68]. This curve is called the diffusion path and is considered to be a characteristic of the diffusion couple. The PPM treatment predicts that the location of the ZFP is determined by complex factors such as the relative magnitudes of fluxes of constituent elements rather than by clear-cut thermodynamic factors. However, an indirect but close relationship exists between intersection points of diffusion paths and isoactivity lines drawn through the terminal alloys, and the locations of the ZFP as predicted by Dyananda [68]. Although this work essentially confirms the general predictions of the phenomenological approach, this is the first attempt to identify the microscopic contents of such empirical concepts as the diffusion path and zero-flux plane.

Although the PPM has proved to be very versatile in dealing with a variety of kinetic problems, some unsatisfactory features have been found regarding the calculation of the correlation factor. This is, as mentioned earlier, a consequence of the inherent time correlation problem in the PPM in following individual particle motion. In fact, the method has been found to be very reliable when the change of macro-variables such as the degree of long-range order which is homogeneous in space is followed. However, because the technique of equilibrium statistical mechanics, in which time is not a concern, is utilized to derive time-dependent variables, there is a limitation in its scope of applications. Sato has determined a way [12, 13, 71] to correct this problem within the pair approximation by introducing so-called "time" and "instantaneous distribution" conversions. These conversions produce results with the same degree of approximation as that in the homogeneous case, and agree very well with other calculations [12, 13]. One serious limitation of these conversion schemes, however, is that their generalization beyond the pair approximation is not possible in a simple fashion.

Calculation of the correlation factor using the kinetic equation approach of Allnatt and co-workers [72–74] shows similar features as the PPM. Fig. 6 has been reproduced from [72], where the solid lines are based on Manning's random alloy model which is known to be close to being exact. The dashed lines are the results of the kinetic equation approach which show a systematic deviation from Manning's results. The approximations become increasingly inaccurate as the difference in the jump rates are increased, and do not give the expected percolation threshold behaviour characteristic of extreme jump-rate ratios.

Calculations using the original PPM exhibit very similar deviation as shown in Fig. 7 ([12]). However, once Sato's "time" conversion is introduced into the PPM, the results (solid lines) approach Manning's results. Similar improvements have also been reported in the kinetic equation approach based on a particular method of decoupling of hierarchy of equations [74]. The decoupling is based on an approximation which

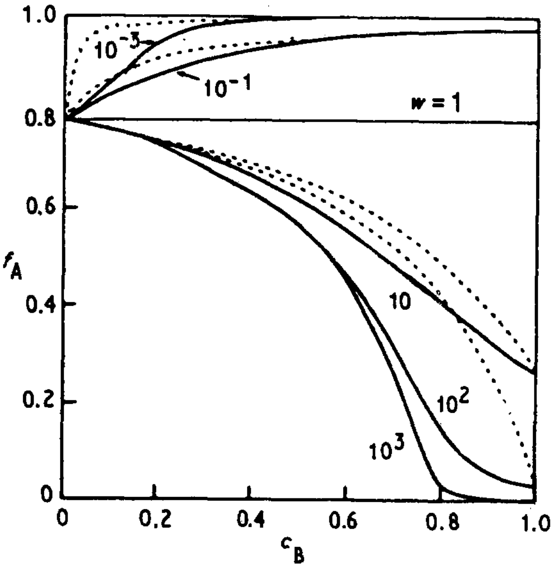

Figure 6 The correlation factor f_A as a function of the concentration of B atoms for an fcc A–B alloy with jump frequency ratios ($w = w_A/w_B$) as marked. (———) Manning's results, (– – –) based on the kinetic equation theory [71].

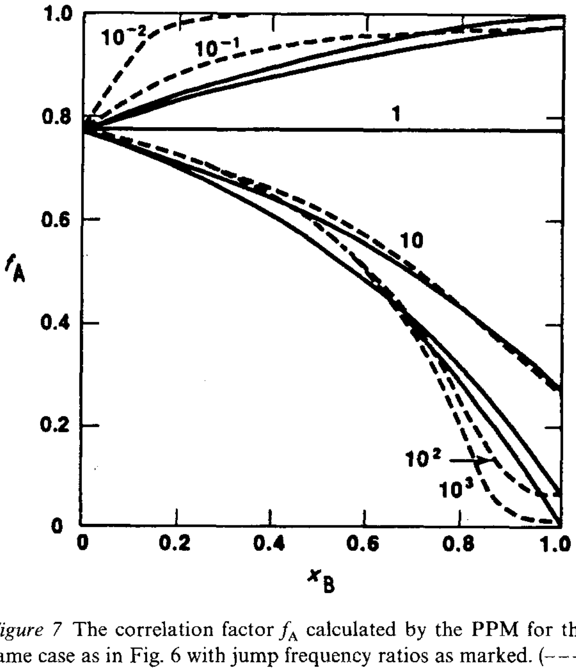

Figure 7 The correlation factor f_A calculated by the PPM for the same case as in Fig. 6 with jump frequency ratios as marked. (– – –) The original PPM results, (———) produced by introducing the time conversion into the PPM [12].

relates terms of third-order to terms of second-order in fluctuations in the occupancies of the sites.

These remarkable similarities in the results of the PPM and the kinetic equation approach may be useful in understanding the fundamental nature of the so-called time correlation problem. Is this an inherent problem of the PPM, or is it a consequence of the approximations due to the size of the basic cluster? It would be a worthwhile effort to extend the PPM calculation of the correlation factor beyond the pair approximation. Such calculations may also give us some clue about the fundamental justification of Sato's conversion schemes.

It is important to recognize where the PPM stands in relation to other methods in diffusion theory such as the well-known pair-association method (PAM of Lidiard [4]). The PAM has specifically been designed for dilute alloys and extensive calculations have been made with great success [75]. However, this technique cannot treat time-dependent many-body problems such as diffusion in highly defective systems and concentrated alloys [76]. On the other hand, the PPM was formulated to deal specifically with these problems. The PPM certainly makes use of some of the strategy of the PAM, and to this extent may be viewed as a generalization of that method.

Recently, efforts have been made to compare the PPM as a kinetic technique with other methods such as the master equation method (MEM) adopted in irreversible statistical mechanics [5]. In the point and the pair approximations, both methods lead to identical results [10, 77], while they vary in the triangle approximation. Although at this stage it is difficult to judge the superiority of one method over the other, the PPM has some specific advantages. Because the PPM has its equilibrium analogue, the CVM, it is physically more tractable, and the degree of approximations can be systematically improved.

Computer simulation such as the Monte-Carlo method (MCM) has found widespread applicability in transport problems [6, 57], yet the need for an analytical treatment such as the PPM remains. Without an appropriate theoretical framework, the computer simulation results are difficult to interpret. On the other hand, due to approximations involved, results of the analytical treatments are not exact. In fact, analytical treatment and computer simulation are essentially complementary, and the PPM calculations have been found to agree well with the MCS results [13, 78–82].

5. Conclusion

The path probability method (PPM) represents a systematic analytical technique for dealing with kinetics of cooperative systems. The importance of such a treatment is to gain an overall understanding of the phenomena at an atomistic level, but not necessarily in obtaining exact quantitative assessments. This approach essentially serves as a complement to the phenomenological treatment of irreversible thermodynamics and the other atomic theories. Even with its present limitations, this method is by far the most comprehensive technique available for dealing with atomic transport in such complex cases as highy defective solids, and multicomponent interacting systems. It is anticipated that the PPM in conjunction with other atomic theories of diffusion will continue to make a major impact on our understanding of the complex phenomenon of many-body diffusion.

Acknowledgements

The author thanks Professor G. E. Murch, University of Newcastle, Australia, and Professor A. B. Lidiard, AERE, Harwell, UK, for valuable comments on the manuscript.

References

1. N. L. PETERSON, in "Solid State Physics", Vol. 22, edited by F. Seitz, D. Turnbull and H. Ehrenreich (Academic Press, New York, 1968) p. 409.
2. A. D. Le CLAIRE, in "Physical Chemistry (Solid State)", Vol. 10, edited by H. Eyring, D. Henderson and W. Jost (Academic Press, New York, 1970) p. 261.
3. J. R. MANNING, "Diffusion Kinetics for Atoms in Crystals" (Van Nostrand, New York, 1968).
4. A. B. LIDIARD, *Phil. Mag.* **46** (1955) 1218.
5. N. G. van KAMPEN, in "Fluctuation Phenomena in Solids", edited by R. E. Burgess (Academic Press, New York, 1965) p. 139.
6. G. E. MURCH and S. J. ROTHMAN, in "Nontraditional Methods in Diffusion", edited by G. E. Murch, H. K. Birnbaum and J. R. Cost (TMS, Warrendale, PA, 1984) p. 281.
7. R. KIKUCHI, *Prog. Theor. Phys. (Kyoto) Suppl.* **35** (1966) 1.
8. H. SATO, in "Nontraditional Methods in Diffusion", edited by G. E. Murch, H. K. Birnbaum and J. R. Cost (TMS, Warrendale, PA, 1984) p. 203.
9. R. KIKUCHI, *Phys. Rev.* **81** (1951) 988.
10. T. ISHIKAWA, K. WADA, H. SATO and R. KIKUCHI, *ibid.* **A33** (1986) 4164.
11. R. KIKUCHI, private communication (1989).
12. H. SATO and R. KIKUCHI, *Phys. Rev.* **B28** (1983) 648.
13. H. SATO, S. A. AKBAR and G. E. MURCH, in "Diffusion in Solids: Recent Developments", edited by M. A. Dayananda and G. E. Murch (TMS, 1985) p. 67.
14. R. KIKUCHI, T. ISHIKAWA and H. SATO, *Physica* **123A** (1984) 227.
15. T. ISHIKAWA, S. A. AKBAR, W. ZHU and H. SATO, *J. Amer. Ceram. Soc.* **71** (1988) 513.
16. S. A. AKBAR, M. KABURAGI, H. SATO and R. KIKUCHI, *ibid.* **70** (1987) 246.
17. S. A. AKBAR and H. SATO, in "Oxidation of Metals and Related Mass Transport", edited by M. A. Dayananda, S. J. Rothman and W. E. King (TMS, Warrendale, PA, 1987) p. 49.
18. S. A. AKBAR, M. KABURAGI and H. SATO, *J. Phys. Chem. Solids* **48** (1987) 579.
19. K. WADA, A. SUZUKI, H. SATO and R. KIKUCHI, *ibid.* **46** (1985) 1195.
20. T. ISHIKAWA, H. SATO, R. KIKUCHI, S. A. AKBAR, W. ZHU and A. S. DATTA, in preparation.
21. H. SATO and R. KIKUCHI, *J. Chem. Phys.* **55** (1971) 677.
22. R. KIKUCHI and H. SATO, *ibid.* **55** (1971) 702.
23. H. SATO and R. KIKUCHI, in "Superionic Conductors", edited by G. D. Mahan and W. L. Roth (Plenum Press, New York, 1976) p. 135.
24. R. KIKUCHI and H. SATO, in "Superionic Conductors", edited by G. D. Mahan and W. L. Roth (Plenum Press, New York, 1976) p. 167.
25. H. SATO and R. KIKUCHI, *J. Physique* **38 C7** (1977) 159.
26. H. SATO, in "Solid Electrolytes", edited by S. Geller (Springer-Verlag, 1977) p. 3.
27. H. SATO and R. KIKUCHI, in "Fast Ion Transport in

Solids", edited by P. Vashista, J. N. Mundy and G. K. Shenoy (North Holland, Amsterdam, 1979) p. 337.
28. H. SATO and K. GSCHWEND, *Phys. Rev.* **B22** (1980) 4626.
29. H. SATO, *Solid State Ionics* **5** (1981) 183.
30. A. SUZUKI, H. SATO and R. KIKUCHI, *Phys. Rev.* **B29** (1984) 3550.
31. T. ISHIKAWA and H. SATO, in "Superionic Solids and Solid Electrolytes: Recent Trends", edited by A. L. Laskar and S. Chandra (Academic Press, New York, 1989) p. 439.
32. R. KIKUCHI and H. SATO, *J. Chem. Phys.* **51** (1969) 161.
33. *Idem., ibid.* **53** (1970) 2702.
34. *Idem., ibid.* **57** (1972) 4962.
35. H. SATO and R. KIKUCHI, in "Mass Transport Phenomena in Ceramics, Materials Science Research", edited by A. R. Cooper and A. H. Heuer (Plenum Press, New York, 1975) p. 149.
36. H. SATO, T. ISHIKAWA and R. KIKUCHI, *J. Phys. Chem. Solids* **46** (1985) 1361.
37. T. ISHIKAWA, H. SATO, R. KIKUCHI and S. A. AKBAR, *J. Amer. Ceram. Soc.* **68** (1985) 1.
38. S. A. AKBAR and H. SATO, *J. Phys. Chem. Solids* **50** (1989) 729.
39. H. SATO, A. SUZUKI and R. KIKUCHI, *Solid State Ionics* **9, 10** (1983) 725.
40. H. SATO, K. WADA, A. SUZUKI and S. A. AKBAR, *ibid.* **18, 19** (1986) 178.
41. H. SATO, S. A. AKBAR and T. ISHII, *ibid.* **28–30** (1988) 138.
42. J-S. CHOI, M. SARIKAYA, I. A. AKSAY and R. KIKUCHI, *Phys. Rev.* **B42** (1989) 4244.
43. H. SATO, K. GSCHWEND and R. KIKUCHI, *J. Physique* **38 C7** (1977) 357
44. K. GSCHWEND, H. SATO and R. KIKUCHI, *J. Chem. Phys.* **69** (1978) 5006.
45. K. GSCHWEND, H. SATO, R. KIKUCHI, H. IWASAKI and H. MANIWA, *ibid.* **71** (1979) 2844.
46. J. K. McCOY, R. KIKUCHI, K. GSCHWEND and H. SATO, *Phys. Rev.* **B25** (1982) 1734.
47. S. FUKUDA, PhD thesis, University of Washington, Seattle, WA (1988).
48. K. WADA, M. KABURAGI, T. UCHIDA and R. KIKUCHI, *J. Stat. Phys.* **53** (1988) 1081.
49. K. WADA, H. TSUCHINAGA and T. UCHIDA, in "Dynamics of Ordering Processes in Condensed Matter", edited by S. Komura and H. Furukawa (Plenum, New York, 1988) p. 29.
50. T. UCHIDA, F. SATO and K. WADA, "Kinetics of Crystal Growth on the SOS Model", preprint (1990).
51. H. SCHMALZRIED, W. LAQUA and P. L. LIN, *Z. Naturforsch* **34a** (1978) 192.
52. H. SCHMALZRIED and W. LAQUA, *Oxid. Metals* **15** (1981) 339.
53. H. K. BOWEN, in "Materials Science in Energy Technology", edited by G. G. Libowitz and S. M. Whitingham (Academic Press, New York, 1979).
54. J. MIZUSAKI, W. R. CANNON and H. K. BOWEN, *J. Amer. Ceram. Soc.* **63** (1980) 391.
55. M. N. MENON, S. M. COPLEY and B. A. TROESCH, *Acta Metall.* **23** (1975) 199.
56. W. T. PETUSKEY and H. K. BOWEN, *J. Amer. Ceram. Soc.* **64** (1981) 611.
57. G. E. MURCH, in "Diffusion in Crystalline Solids", edited by G. E. Murch and A. S. Nowick (Academic Press, 1984).
58. G. E. MURCH and J. C. DYRE, *CRC Crit. Rev. Solid State Mater. Sci.* **15** (1989) 345.
59. S. A. AKBAR, *J. Mater. Sci.* (1992) in press.
60. T. ISHII, H. SATO and R. KIKUCHI, *Phys. Rev.* **B34** (1986) 8335.
61. J. O. ISARD, *J. Non-Cryst. Solids* **1** (1969) 235.
62. D. E. DAY, *ibid.* **21** (1976) 343.
63. J. A. BRUCE, R. A. HOWIE and M. D. INGRAM, *Solid State Ionics* **18, 19** (1986) 1129.
64. L. M. FOSTER, M. P. ANDERSON, G. V. CHANDRASEKHAR, G. BURNS and R. B. BRADFORD, *ibid.* **5** (1981) 215.
65. M. P. ANDERSON and L. M. FOSTER, *ibid.* **5** (1981) 219.
66. J. L. BRIANT and G. C. FARRINGTON, *ibid.* **5** (1981) 207.
67. J. A. BRUCE and M. D. INGRAM, *ibid.* **9, 10** (1983) 717.
68. M. A. DAYANANDA and C. W. KIM, *Metall. Trans.* **10A** (1979) 1333.
69. C. W. KIM and M. A. DAYANANDA, *ibid.* **14A** (1983) 857.
70. M. A. DAYANANDA, in "Diffusion in Solids: Recent Developments", edited by M. A. Dayananda and G. E. Murch (TMS, Warrendale, PA, 1985) p. 195.
71. H. SATO, *JIM* **32** (1991) 509.
72. Y. OKAMURA and A. R. ALLNATT, *Phil. Mag. A* **54** (1986) 773.
73. L. K. MOLEKO, Y. OKAMURA and A. R. ALLNATT, *J. Chem. Phys.* **88** (1988) 2706.
74. L. K. MOLEKO, A. R. ALLNATT and E. L. ALLNATT, *Phil. Mag. A* **59** (1989) 141.
75. A. D. Le CLAIRE, *J. Nucl. Mater.* **69/70** (1978) 70.
76. G. E. MURCH, "Atomic Diffusion Theory in Highly Defective Solids, Diffusion and Defects", Monograph Series, No. 6, edited by Y. Adda, A. D. Le Claire, L. M. Slifkin and F. H. Wohlbier (Trans Tech., Aedermansdorf, 1980).
77. K. WADA, T. ISHIKAWA, H. SATO and R. KIKUCHI, *Phys. Rev.* **A33** (1986) 4171.
78. L. ZHANG, M. GURR and G. E. MURCH, in "Ceramic Developments, Materials Science Forum", Vols **34–36** edited by C. C. Sorrell and B. Ben-Nissan (Trans Tech., Aedermansdorf, 1988) p. 807.
79. G. E. MURCH and L. ZHANG, *J. Aust. Ceram. Soc.* **25** (1989) 9.
80. L. ZHANG and G. E. MURCH, *Phil. Mag.* **A62** (1990) 267.
81. G. E. MURCH and L. ZHANG, in "Diffusion in Materials", Vol. 179, edited by A. L. Laskar, L. J. Bocquet, G. Brebeck and C. Monty, NATO ASI Series (Kluwer Academic, Boston, 1990) p. 251.
82. L. ZHANG and G. E. MURCH, *Solid State Ionics* (1991) in press.

Received 24 September
and accepted 26 September 1991