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DOE/ER/10913-3

**MULTICOMPONENT DIFFUSION UNDER GENERAL
CHEMICAL POTENTIAL GRADIENTS**

**Final Report
Period July 1, 1981 - June 30, 1984**

DOE/ER/10913--3

DE84 010830

**Hiroshi Sato and Ryoichi Kikuchi
School of Materials Engineering
West Lafayette, Indiana 47907**

June 1984

MASTER

Prepared For

**U.S. Department of Energy
Under Contract No. DE-AC02-81ER10913. A002**

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2. Application of the Path Probability Method to
Transport Phenomena
3. Demixing of Materials Under Chemical Potential
Gradients

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ABSTRACT

Theoretical basis for identifying the origin of deterioration of high temperature materials by diffusion has been sought. The need for an appropriate form of irreversible statistical mechanics, rather than commonly utilized irreversible thermodynamics, to this problem was identified. The Path Probability method of irreversible statistical mechanics was thus adapted to diffusion problems and necessary modifications of the method suitable for transport problems in multicomponent systems were made. Thermal diffusion (diffusion which occurs under temperature gradient) was then formulated by the Path Probability method for the first time, and so far elusive concepts such as the heat of transport were thus microscopically identified. An example of demixing of originally homogeneous solid solutions under general chemical potential gradients was thus worked out.

A considerable amount of progress with respect to the application of the PPM to transport problems has been made since we launched the present program. A brief outline of the progress in the application of the PPM to general transport problems is given by H. Sato in his review article "Application of the Path Probability Method to Transport Problems" in "Nontraditional Methods in Diffusion" which published as a TMS-AIME Conference proceedings volume. In the following, progress made since the inception of the present research program is summarized.

1. Formulation of Materials Transport Under General Chemical Potential

Gradients in Multicomponent Systems.

In order to deal with decomposition of materials, it is necessary to derive the Onsager equation for diffusion under the most general condition. Because of this situation, we have reorganized the formulation of the problem.

In most applications, it is necessary to derive the Onsager equation under the steady state condition, a condition which requires that the distribution of atoms and the flow do not change with time.¹

Diffusion problems in a crystalline solid under driving forces in one direction are treated. Constituent atoms (ions) are assumed to be interacting with other atoms at the nearest neighboring distance. The flow is calculated as the difference in atomic jumps across a unit cross section of a reference plane perpendicular to the direction of the driving forces. Because of interactions, atoms in the crystal take a certain distribution. The distribution of atoms can thus be calculated by the CVM. In the linear range in which the Onsager equation is valid, the driving force does not disturb the distribution. Atoms can migrate through vacant, available sites of the crystal. The probabilities of jumps of atoms which depend on the distribution of atoms are then calculated by the PPM. The difference of jumps in the direction of the driving forces and

those in the reverse direction thus represents the flow.

A straightforward application of the PPM under the given condition in the linear range leads to an equation for a normalized flow Ψ_i of the i -th species.

$$\Psi_i = -\dot{\alpha}_i + \sum_j Q_j \psi_{ji} \quad (1)$$

Here, Ψ_i times the jump frequency of the i -th species indicates the flow of an atom of i -th species. The first term indicates the random walk of an atom of the i -th species under the driving force of $\dot{\alpha}_i$. The factor Q_j indicates the distribution of the j -th species (determined by the CVM) at the nearest neighboring site of the i -th atom, and ψ_{ji} indicates the deviation of j - i pair from the equilibrium distribution under the applied driving forces (and is proportional to the driving forces). In other words, the second term indicates the flows of atoms which depend on the distribution of atoms. By utilizing the specific expression of ψ_{ji} (by the use of the steady state condition), we can thus obtain the Onsager equation for diffusion

$$\Phi_i = L_{i1} \dot{\alpha}_1 + L_{i2} \dot{\alpha}_2 + \cdots + L_{in} \dot{\alpha}_n \quad (2)$$

$$(i = 1, 2, \cdots n)$$

and

$$L_{ij} = L_{ji}$$

It is thus clear that the matrix elements, L_{ij} 's, are obtained analytically and that these are independent of the nature of the driving force. These L_{ij} 's have been derived under general conditions up to ternary systems.² The term $\sum_j Q_j \psi_{ji}$ indicates how the motion of the i -th species deviates from random walk and determines the character of transport depending on the properties of the system and the boundary conditions.

The chemical potential diagram which depends on the distribution of atoms can be derived in a straightforward fashion by the CVM if the interaction potentials among atoms are given. Chemical potential maps of ternary systems have thus been calcu-

lated for all Meijering Categories.³ More details are found in the following.

H. Sato and R. Kikuchi, "Theory of Many-Body Diffusion by the Path Probability Method: Conversion From the Ensemble Averaging to the Time Averaging," *Physical Review*, B28 648 (1983).

H. Sato, "The Application of the Path Probability Method to Transport Phenomena", in *Nontraditional Methods in Diffusion*, edited by G. E. Murch, H. K. Birnbaum, and J. R. Cost, TMS-AIME Conference Proceedings Volumes, pp. 203-235 (1984).

H. Sato and R. Kikuchi, Progress Report DOE/ER/10913-2 (1983).

2. Thermal Diffusion

In most cases, the Onsager equation for diffusion is treated under the isothermal condition. However, one of the important causes for the deterioration of materials at high temperatures is due to thermal diffusion or transport of materials under the existence of temperature gradient. At the same time, there is a flow of heat or energy along with the flow of materials. The exact content of heat (energy) of transport is sometimes a matter of dispute. Because of these reasons, we decided to derive the Onsager equation under the coexistence of chemical potential gradients and a temperature gradient in multicomponent systems.⁴

The formalism of the PPM allows the treatment of transport of atoms under a temperature gradient in a similar fashion to that of isothermal diffusion problems as long as the concept of local temperature can be adopted. Since the conjugate variable of temperature gradient (in terms of β where $\beta = 1/kT$) is the energy flow, the Onsager equation for two component systems takes the form

$$\begin{aligned}\Phi_1 &= -L_{11}\dot{\alpha}_1 - L_{12}\dot{\alpha}_2 + L_{13}\dot{\beta} \\ \Phi_2 &= -L_{21}\dot{\alpha}_1 - L_{22}\dot{\alpha}_2 + L_{23}\dot{\beta} \\ \Phi_3 &= -L_{31}\dot{\alpha}_1 - L_{32}\dot{\alpha}_2 + L_{33}\dot{\beta}\end{aligned}\tag{3}$$

Suffices 1 and 2 indicate two species of atoms and 3 indicates the energy. It is also to

be noted that $\alpha_i = \beta\mu_i$. The first two equations are for particle flows and can readily be obtained by the application of the PPM. The third equation, however, is obtained separately by calculating the entropy production of the system under the temperature gradient. The Onsager reciprocity relations with respect to the energy flow

$$L_{13} = L_{31}$$

and

$$L_{23} = L_{32} \quad (4)$$

follow from these calculations, indicating the internal consistency of the treatment. The L_{33} term represents the heat conductivity of the system associated with the particle flow (excluding the heat conduction through phonons, electrons, etc.). The formalism of the CVM - PPM thus allows the expressions of L_{31} , L_{32} and L_{33} in closed forms.

The analysis of $L_{i3}(=L_{3i})$, for example, shows that the energy carried by a particle of the i -th species due to its transport is given by a quantity

$$U_i + \varepsilon_i^*$$

where U_i is the activation energy of motion of a particle of the i -th species and ε_i^* is an average of the pair interaction energy of a particle of the i -th species and is given by

$$\varepsilon_i^* = \varepsilon_{i1}Q_1 + \varepsilon_{i2}Q_2.$$

Here ε_{ij} specifies the pair interaction energy between the i -th species and the j -th species and Q_1 and Q_2 specify the amount of each species of surrounding particles. The quantities U_i and ε_i^* thus represent the kinetic energy and the potential energy, respectively, carried by a particle of the i -th species. The flow of entropy (heat) can also be calculated from these expression which includes the flow of chemical potential of the i -th species.

The demixing of constituent species due to thermal diffusion is known as the Soret effect.⁵ If the Soret effect occurs in ionic conductors, the demixing is related to the thermoelectric effect. A detailed treatment of these effects is proposed. The demixing is generally counterbalanced by the appearance of opposing chemical potential gra-

dients. The detail of the treatment is found in

H. Sato and R. Kikuchi, Progress Report DOE/ER/10913-2 (1983).

R. Kikuchi, T. Ishikawa, and H. Sato, "Statistical Mechanics of Thermal Diffusion," *Physica* 123A, pp. 227-252 (1984).

3. Demixing

If placed under chemical potential gradients at high temperatures, a demixing of originally homogeneous solid solutions occurs if the diffusion coefficients of constituent components are different. This is a source of deterioration of high temperature materials. This work is to show, under special boundary conditions, how such demixing can take place.

Because the Onsager equation for diffusion for multicomponent systems has been derived under general conditions (see 1.) the problem can be solved if appropriate boundary conditions can be given.

In order to deal with the problem of demixing, it is necessary to treat a finite system and to give appropriate boundary conditions with respect to the disposal (supply and loss) of materials. It would be especially rewarding if one can find such boundary conditions which would lead to a steady state. Schmalzried et al. have demonstrated that, in the problem of demixing of binary oxide systems under an oxygen partial pressure gradient, such simplifying boundary conditions can be found.⁵⁻⁶ In order to show the effect of demixing, therefore, similar assumptions were adopted in our derivation.

Let us consider a binary solid solution of divalent metal oxides such as (Co, Mg)O. These oxides crystallize into the NaCl type structure and metal ions occupy the lattice sites of the fcc structure (octahedral sites). Because of the ease of mathematical handling, a hypothetical oxides in which metal ions occupy the lattice sites of the bcc structure is treated. As long as we deal with disordered (no ordering in distribution

among two kinds of metal ions), this simplification is not expected to create any essential change in diffusion characteristics. We further assume that oxygen ions are immobile, form a rigid lattice and provide lattice sites for metallic ions. Metal ions are assumed to move via vacancy mechanism.

Actual calculations were made for a binary system. The Onsager equations under a uniform temperature are thus given by

$$\begin{aligned}\Phi_1 &= -L_{11}\dot{\alpha}_1 - L_{12}\dot{\alpha}_2 \\ \Phi_2 &= -L_{21}\dot{\alpha}_1 - L_{22}\dot{\alpha}_2\end{aligned}\tag{b}$$

$$L_{12} = L_{21}$$

We treated the case in which no mutual interactions among atoms (ideal solution) exist. Introduction of mutual interactions does not introduce any essential difference. The existence of the cross terms, L_{12} and L_{21} , was noted even under such an idealized condition and its contribution amounts to ~10%.

The existence of the oxygen partial pressure difference creates the vacancy concentration gradient for metal ions. The calculation was made by fixing the vacancy concentrations at the both ends. The concentration gradient of vacancies in the system induces the vacancy flow or the diffusion of both kinds of metal ions. If metal ions diffused to the end react with oxygen ions to form the same kind of oxide, the concentration of constituent ions at the end surface of the crystal remains constant in order to maintain the equilibrium with the oxygen gas under the uniform temperature, although the crystal surfaces move in the direction of the gradient with respect to the laboratory system fixed at the oxygen lattice. The concentration gradients of metal ions thus created tend to oppose the flow of metal ions. Under the steady state condition, the crystal moves with a constant speed with respect to the laboratory system, keeping the concentration profiles of cations time-independent. The task is then to

calculate the time independent concentration profile.⁷

The detail of the calculation is given in

H. Sato and R. Kikuchi, Progress Report DOE/ER/10913-2, Jan. 31, 1983, T. Ishikawa, H. Sato, R. Kikuchi, and S. A. Akbar, "Demixing of Materials Under a Chemical Potential Gradients". To be published.

4. Correlation Factor in Multicomponent Systems

The correlation factor was initially introduced as the ratio of the tracer diffusion coefficient D_T and the self diffusion coefficient D_S as

$$D_T/D_S = f \quad (6)$$

so that the value of D_S could be evaluated from the measurement of D_T .^{8,9} Theoretically, on the other hand, f is defined as the ratio of the drift motion or the diffusion coefficient of a single atom in the assembly and that represented by the random walk, D_R .^{10,11} The two definitions agree in the case of self diffusion in nearly perfect crystals, because in this case $D_S = D_R$. However, in a general case of diffusion, the former depends on the boundary conditions of measurements. The situation is not well appreciated and is, at most, treated in the formalism of irreversible thermodynamics. An advantage of the PPM is that the Onsager equation for diffusion can be derived analytically so that the relation between measurable quantities can be unambiguously derived. As a simplest possible case to examine the relations, therefore, we investigated the diffusion coefficient of isotopes as a function of the composition of isotope atoms.

The Onsager equation for a two component system is given as

$$\Phi_1 = -L_{11}\dot{\alpha}_1 - L_{12}\dot{\alpha}_2$$

$$\Phi_2 = -L_{21}\dot{\alpha}_1 - L_{22}\dot{\alpha}_2 \quad (7)$$

$$L_{12} = L_{21}$$

The constituent 2 is assumed to be the isotope of 1 and therefore no effective interaction (interaction potentials between atomic pairs are the same) between 1 and 2 is assumed. Furthermore, the jump frequencies of these two constituents should be equal. The calculation of the diffusion coefficient was made under the following three different conditions.

- a. In measuring Φ_2 , we first impose a condition $\dot{\alpha}_1 = 0$. The case is equivalent, for example, to measuring the ionic conductivity of the species 2 as if only the species 2 has a charge. If such an experimental condition can be realized, the flow of Φ_2 is then represented by

$$\Phi_2 = -L_{22}\alpha_2 \quad (8)$$

- b. We assume the existence of the condition

$$x_1 + x_2 = 1$$

where x_1 and x_2 are the composition of the species 1 and 2, respectively. From this

$$\dot{x}_1 = -\dot{x}_2$$

follows. In addition, we assume the Gibbs-Duhem relation

$$x_1\dot{\alpha}_1 = -x_2\dot{\alpha}_2 \quad (9)$$

Such a condition is often assumed in the treatment of diffusion.^{12,13} Under these conditions, Φ_2 can be expressed in terms of $\dot{\alpha}_2$.

- c. The Onsager equation shown above is derived under a steady state condition so that finite amounts of flows, Φ_i 's, exist in the system. The appearance of the cross terms in systems without interactions among atoms in Eq. (17) is due to this fact. Because there are no interactions among atoms, there should be no physical correlation between the two species. If Φ_i 's are evaluated under the condition that no cross terms appear, then Φ_i 's represent the drift motion of the assembly of i -th species, etc. multiplied by the driving force. The ratio of diffusion coefficient D_T

obtained from Φ_2 to D_R can be defined as the correlation factor.

The dependence of the correlation factor f on the concentration of isotope atoms thus defined for these three different cases is shown in Fig. 1.

The details of the treatment are shown in

H. Sato and R. Kikuchi: Progress Report DOE/ER/10913-2, Jan. 31, 1983, and will be published shortly as H. Sato, T. Ishikawa and R. Kikuchi, "Correlation Factor of Tracer Diffusion for Large Tracer Concentrations." (in preparation.)

5. Time Conversion

Based on the formalism of the PPM, Eq. (1) indicates the differential equation with respect to time t , (Ψ_i is expressed in terms of path variables and, hence, represents the time dependence of state variables) and Q_i specifies the distribution of atoms at a time instant t determined by the CVM. Therefore, the flow evaluated by the PPM is the flow at a time instant. In other words, in terms of frequency dependent conductivity $\sigma(\omega)$, that evaluated by the PPM in principle corresponds to $\sigma(\infty)$. On the other hand, what we usually require is the knowledge of $\sigma(0)$. Because of this situation, the relation between $\sigma(\infty)$ and $\sigma(0)$ was sought under the formalism of the PPM. In the linear range in which the Onsager equation for diffusion is valid, it was found to be possible to convert $\sigma(\infty)$ into $\sigma(0)$ without changing the nature of approximation. The problem concerned here was essentially the conversion of the ensemble average of flow at a time instant to the time average in a single system. The background of this work, however, was the examination of the formalism of the Path Probability method itself. The detail of the treatment is given in

H. Sato and R. Kikuchi, "Theory of Many-Body Diffusion by the Path Probability Method: Conversion from Ensemble Averaging to Time Averaging," Phys. Rev. **B28** 648 (1983).

Fig. 1 Dependence of the correlation factor on the concentration of tracer atoms calculated under three different boundary conditions.
a) $\dot{\alpha}_1 = 0$.
b) $x_1 \dot{\alpha}_1 = -x_2 \dot{\alpha}_2$ (Gibbs-Duhem relation).
c) $\dot{\alpha}_1 = 0, L_{12} = 0$.

6. Instantaneous Distribution

Physically, the flow Ψ_i in Eq. (1) should represent the statistical average of the time correlation of individual particles. In other words, a flow should represent the average of the motion of individual particles. Based on the CVM-PPM formalism given in Eq. (1), Q_j should represent the average of the distribution of atoms at time t (evaluated by the CVM). However, the distribution Q_j evaluated by the CVM corresponds to that of the equilibrium state and does not include t . Moreover, it is represented in the form of average. Therefore, the flow Ψ_i given in Eq. (1) represents the time correlation of the averaged state, or that in terms of the state variables rather than the average of the time correlations of individual particles. The conversion to the latter can, however, be made by evaluating the flow in a single system rather than utilizing the ensemble of systems adopted by the CVM-PPM approach. The conversion was made successfully but with some degree of simplification. The major change created by the conversion is the appearance of the physical correlation factor f_i (or the percolation efficiency^{13,14} which is explained later) in the disordered state with short range order in the distribution of atoms. In the CVM-PPM formalism, f_i appeared only when the system had to be divided into sublattices (due to the existence of the long range order).^{15,16}

In Fig. 2, a comparison of results before and after the conversion is given for the calculation of the correlation factor for β'' -alumina. Here, the dependence of the tracer correlation factor for conduction ions on the two dimensional honeycomb lattice is calculated as a function of the occupancy rate among the available sites of conduction ions. The occupancy rate is given as the ratio of the total number of conduction ions and the total number of available sites. Because repulsive interactions among nearest neighboring conduction ions, ε , are assumed, the conduction ions tend to take an ordered arrangement at low temperatures. At temperature $kT/|\varepsilon| = 0.3$, at which the calculation is made, the system is in the ordered state. The curves in A are before

Fig. 2 Composition dependence of the correlation factor of disordered (D) and ordered (O) β'' -alumina at $\frac{kT}{|\varepsilon|} = 0.3$. $|\varepsilon|$ indicates the magnitude of the interaction between the nearest neighboring pair of conduction ions and is used to normalize the temperature (Ref. 16).

A) Original PPM.
a: original PPM (Ref. 16). (ordered state added)
b: original PPM with the time conversion

B) Original PPM with the instantaneous distribution correction
a: original PPM with the instantaneous distribution correction
b: original PPM with the instantaneous distribution correction and with the time conversion

the conversion and the curves in B are after the conversion. Although the qualitative behavior is more or less the same in both cases, the difference is nevertheless noteworthy. Most remarkable difference by conversion is noticed for the disordered state. The correlation factor for the disordered state is calculated by artificially keeping the long range order parameter zero. The dip of the correlation factor near the composition 0.5 in B is due to the dip of f_l as a consequence of the development of the short range order. The result after the conversion in B agrees well with the result of a computer simulation for a correspondent case by Murch et al.^{17,18} The background of this work was, along with the problem of time conversion, the examination of the formalism of the PPM itself. The results are not published yet, but some details of the treatment is found in

H. Sato, The Application of the Path Probability Method to Transport Phenomena, TMS-AIME Conference Proceedings "Nontraditional Methods in Diffusion", edited by G. E. Murch, H. K. Birnbaum and J. R. Cost, (1984)

7. The Percolation Efficiency and the Mixed Alkali Effect in β Aluminas and in Glasses

One of noteworthy features found in the calculation of ionic conductivity by the PPM is the appearance of the "physical correlation factor f_l " in the same sense as that the correlation factor appears in the tracer diffusion coefficient.^{13,14,17} The existence of such a factor in the ionic conductivity had been unknown earlier. The physical correlation factor is sometimes called the charge correlation factor for this reason and, at present, is one of central interests among theoretical problems in transport processes. The existence of f_l is traced to the existence of nonvanishing term, $\sum_j Q_j \psi_{ji}$, in Eq. (1). The appearance of nonzero $\sum_j Q_j \psi_{ji}$ in ionic conduction is due to the fact that the conduction path for ions in solid is very limited. Therefore the topology of the conduction path plays an important role in the appearance of ψ_{ji} . The importance of the topology

of the conduction path in the appearance of the percolation efficiency has not yet been realized fully. The appearance of the correlation factor in tracer diffusion is due to, because only the motion of a single atom (of the i -th species) is calculated, the non-symmetry in the statistical weight between i and j which causes the appearance of ψ_{ji} .

The physical correlation factor essentially represents the percolation efficiency of ions determined by the nature of the conduction path in solids. There has been a peculiar phenomenon known as the mixed alkali effect for some time in β -aluminas and in glasses. If a part of alkali ions are replaced by another kind of alkali ions in these systems, the conductivity of the system (due to the alkali ions) drops drastically in the intermediate composition range without any appreciable reasons. In order to understand this phenomenon, we have treated the ionic conductivity of binary systems.^{13,14} If attractive interactions exist among different kinds of ions, ordered arrangements among ions are created in the crystal lattice and f_i decreases drastically. This corresponds to the case in which key sites of conduction paths are blocked by one kind of ions by interactions in glass systems. On the other hand, local motions of ions are not seriously affected by such blocking. Therefore, the blocking effect should vanish at high frequencies at which only local motions contribute to the conduction. The measurement of the frequency dependence of the mixed alkali effect both in β -aluminas¹⁹ and glasses²⁰ indicate that this is true.

The content of 5.-7. concerns the formalism of the PPM. Therefore, a major basis of the problems has so far been worked out in the project "Kinetics of Phase Transitions" supported by National Science Foundation. However, these results (time conversion, instantaneous distribution conversion and the concept of percolation efficiency) have serious consequences in transport problems and, hence, these results will be utilized for further development of this project.

The details of the treatment are found in

H. Sato, A. Suzuki and R. Kikuchi, "A Theoretical Model for Mixed Alkali Effect in Ionic Conduction in β -Aluminas and Glasses," *Solid State Ionics*, 9-10 pp. 725-729 (1983).

A. Suzuki, H. Sato and R. Kikuchi, "Ionic Conductivity in Binary Systems", *Phys. Rev. B29*, pp. 3550-3566 (1984).

8. Diffusion Path

If a diffusion couple is annealed at a high enough temperature, a penetration of components into the other side across the boundary of the couple occurs by diffusion. The penetration profile, if plotted in the concentration diagram, is called the diffusion path. Empirically, the diffusion path has been found to be time independent. Dayananda et al. at Purdue University have found that zero flux conditions can exist between certain elements on the diffusion path and have tried to relate this to thermodynamical properties of the system (zero flux plane). Because the problem is closely connected to the demixing, we tried to relate our theoretical effort to such interesting experimental evidences in ternary systems.

The analysis in ternary systems indicates that the zero flux condition can exist up to two combinations (out of three) of elements, but without any apparent thermodynamical relation. Further, it was not possible for us to confirm the time independence of the diffusion path strictly on a theoretical basis. If the diffusion path is time independent, there should exist a scaling relation with respect to x (diffusion length) and time, t . Customarily $x \sim \sqrt{t}$ relation is assumed in analyzing the data. However, it can quite generally be proved that this type of scaling does not exist in diffusion in multicomponent systems. Our effort is continued with the following two major objectives.

1. If a certain kind of scaling law can exist so that the invariance of the diffusion path with respect to time can be proved; and
2. If zero flux planes can be related to definite thermodynamical relations as long as a quasi time invariance of the diffusion path can be assumed.

A progress report on this subject is found in

H. Sato and R. Kikuchi, Progress Report DOE/ER/10913-2, January 31, 1983.

Publications

1. "Statistical Mechanics of Thermal Diffusion," R. Kikuchi, T. Ishikawa, and H. Sato, *Physica*, **123A**, pp. 227-252 (1984). (A reprint attached.)
2. "Application of the Path Probability Method to Transport Phenomena," H. Sato, in *Nontraditional Methods in Diffusion*, edited by G. E. March, H. K. Birnbaum, and J. R. Cost, TMS-AIME, pp. 203-235 (1984). (A preprint attached, reprints not available.)

In Preparation

1. "Demixing of Materials Under Chemical Potential Gradients," T. Ishikawa, H. Sato, R. Kikuchi, and S. A. Akbar. (A preprint attached.)
2. "Correlation Factor of Tracer Diffusion for a Large Tracer Concentration," H. Sato, T. Ishikawa, and R. Kikuchi.

Related Publications

1. "Theory of Many Body Diffusion By the Path Probability Method: Conversion From Ensemble Averaging to Time Averaging," H. Sato and R. Kikuchi, *Phys. Rev.*, **B28**, 648-664 (1983).
2. "A Theoretical Model for Mixed Alkali Effect in Ionic Conduction in β -Aluminas and Glasses," H. Sato, A. Suzuki, and R. Kikuchi, *Solid State Ionics*, **9-10**, 725-729 (1983).
3. "Ionic Conductivity in Binary Systems," A. Suzuki, H. Sato, and R. Kikuchi, *Phys. Rev. B*, **B29**, 3550-3566 (1984).

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