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Technical Report

Study of Multicomponent Diffusion and Transport Phenomena

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Hiroshi Sato

School of Materials Engineering

Purdue University

West Lafayette, IN 47907

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Technical Report

The grant "Study of Multicomponent Diffusion and Transport Phenomena." (DE-EG02-84ER 45133) started from July 1, 1984, was renewed twice, on July 1, 1987 and July 1, 1990, and then expired on June 30, 1995. During this period, Professor Hiroshi Sato of School of Materials Engineering, Purdue University and Professor Ryoichi Kikuchi of University of California, Los Angeles served as co-principal investigators.

The purpose of this project is to treat the diffusion and transport phenomena in multicomponent systems from an atomistic point of view mainly by means of a kinetic method based on the Cluster Variation Method (CVM)-Path Probability Method (PPM) formalism. As is well known, the CVM has established itself as one of the most systematic methods of statistical thermodynamics and macroscopic phenomena treated by thermodynamics can thus be investigated atomistically in great detail. The advantage of the PPM is that, through the use of the CVM, its formalism is equal to irreversible thermodynamics in dealing with kinetics. Diffusion phenomena are usually dealt with by irreversible thermodynamics. Therefore, complicated multicomponent diffusion phenomena are elucidated by means of the PPM atomistically, in principle, with the accuracy of the CVM. One complication is that, due to its formalism, the PPM corresponds to a mean field approximation as a kinetics. When the system to be treated can be assumed to be homogeneous, this does not create any problem, and the kinetics can be handled accurately with the accuracy of the CVM used. However, if it is applied to transport problems, the degree of approximation as kinetics is lowered to the mean field approximation. However, this trouble can be removed by so-called conversion method if the correction is necessary. The conversion method was developed just before the funding period started.^{18,22,26}

Our involvement in atomistic treatments of diffusion and transport phenomena is long and extensive and the initial effort dates back even before the time this grant started in 1984. Because of this, we first itemize the transport problems treated so far into seventeen categories. The papers published are then listed in chronological order and assembled at the end of the report. The categories listed are almost self-explanatory, but for the projects treated after 1990, some explanations are given. These categories are summarized in the following:

1. Tracer correlation factors in multicomponent systems.^{2,3,6,7,22,25,26}
2. Percolation limit in multicomponent systems (dynamical percolation problems).^{1,2,3,16,17,18,48,50,62}
3. Ionic transport, superionic conduction.^{4,5,7-11,15,16,21,30,40,44}
4. Physical correlation factor and the Haven ratio.^{4,5,7-9,15-17}
5. Conversion of the averaging process of the PPM which converts the PPM from the meanfield approximation to the pair approximation.^{18,22,26}

6. Ionic conductivity in solid electrolytes.^{2-5,9-11,22,25}
7. Diffusion in ordered systems.^{6,10,11,13,14,26,67}
8. Thermal Diffusion Phenomena, Soret Effect.^{20,24,31,32}
9. Demixing in oxides.^{23,33,34,39,43}
10. Diffusion in Semiconductors.
11. Chemical Diffusion Phenomena in alloys and oxides.^{41,43,45,46,51,52,56,63}
12. Diffusion under Stress Gradient.³⁷
13. Possible difference in the Kirkendall effect between metallic alloys and oxides: Soft and rigid lattice gas models.^{43,46}
14. Diffusion paths, and zero flux planes.^{41,45,47,53,54}
15. Percolation efficiency and mixed alkali effect.^{19,27,46,47,49,58,60}
16. Mixed conduction in β -alumina type compounds.^{48,50}
17. Relaxation processes in transport phenomena, frequency dependence of ionic conductivity, and universal dielectric response in disordered solid electrolytes.^{28,29,35,36,61,64-66,68-74}

Since all these subjects are interrelated, the same project is treated from time to time with different emphasis. Since 1993, the relaxation process of the hopping conduction in lattice gas models was almost exclusively treated and we believe that there has been a remarkable progress in this area. Although essential problems have been worked out, a large part of the work has not yet been published. In the following, some details of problems treated after 1990 are explained.

Percolation Threshold in Electronic Conduction β -Alumina Type Solid Electrolytes (Category #16)

The possibility of making β -alumina compounds mixed conducting by the addition of a certain amount of mixed valent ions has been examined from a theoretical point of view using the Cluster Variation Method (CVM). Electronic conductivity in these substances is assumed to be due to the hopping of small polarons to the nearest neighboring ions on the octahedral sites in the spinal block of β -alumina in a manner similar to that in magnetite. The pair approximation of the CVM indicates the composition of the mixed valent ions necessary to induce the electronic conductivity should be at least 0.24 of the number of octahedral sites.⁴⁸ On the other hand, the higher order approximation of the CVM, namely the triangle + extra hedron approximation, increases this number to 0.396,⁵⁰ thereby indicating that an extremely high level of doping would be necessary to render these compounds mixed conducting. The problem belongs to category.¹⁶

Mixed Alkali Effect (Category #15)

The most commonly observed manifestation of the Mixed Alkali effect (MAE) in glasses is the strong minimum observed in the ionic conductivity as one kind of alkali ions is gradually replaced by another, keeping the total alkali content constant. While many attempts have been proposed to explain this phenomenon, no single theory thus far has been completely successful in accounting for its various features, and the problem has remained as one of the outstanding unsolved problems in glass science. However, recent studies, especially the following two features discussed below, indicate that this phenomenon is related to a percolation phenomenon which is characteristic of the ionic conductivity of binary systems with diffusion paths of low connectivity regardless of whether the system is amorphous or crystalline. This is the reason why the study of this phenomenon has been picked up in the present study.

The first evidence is the dependence of the tracer diffusion coefficient of the constituents on composition which show a monotonic decrease as the composition of the other constituent is increased. This is a typical feature of binary systems with attractive interactions between conduction ions of two constituents.^{49,58} The second feature is that the ionic transport behavior very similar to MAE can also be found in β -alumina type compounds with two dimensional diffusion paths. The latter indicates that the essential characteristics of MAE are not in the detail of the structure, but rather are the characteristics of systems whose diffusion (conduction) paths are of low connectivity.^{49,58}

The treatment of ionic conductivity of a binary system with attractive interaction between conduction ions of two constituents clearly showed that the essential feature of the MAE is the very pronounced decrease of the percolation efficiency of the constituent conduction ions. The frequency dependence of conductivity by means of the PPM has been worked out successfully. The strong frequency and temperature dependence of the percolation efficiency f_l explains well the temperature and the frequency dependence of the MAE. The strong concentration dependence of f_l is due to the appearance of a "deep site" created by the short range ordering of constituent conduction ions through mutual interactions. However, in order to explain the proper dependence of f_l on concentration, it was found that the original formalism of the CVM-PPM was not quite appropriate. The characteristic of transport problems is to follow the motion of individual particles and the adoption of the time averaging for the motion of particle is necessary while the CVM-PPM formalism uses the ensemble averaging. Using the conversion processes (Category #5) with respect to the two types of averaging process, it was found the MAE was properly understood by means of the PPM. The conversion process corresponds to the improvement of the mean field approximation of the PPM as kinetics to the pair approximation.

The content of this work was selected as one of the plenary talks at the International Conference on Solid State Ionics held in November, 1989 at Hakone, Japan and was published in the proceedings. Also, a similar content was presented as an invited talk at the American Ceramic Society in 1990 and was published in their proceedings.⁵⁸

Chemical Diffusion Problem

Interdiffusion phenomena which occur between a diffusion couple in multicomponent systems has attracted the attention of many people and a large number of works exist. However, this phenomenon has been a challenge to atomistic treatment until a method is found in terms of lattice gas models for the treatment of the disposal of materials. The Onsager equation for diffusion referring to the equilibrium in multicomponent systems can be defined analytically. By converting chemical potential gradients into concentration gradients, intrinsic diffusion coefficients can be defined analytically as a function of compositions from the Onsager matrix elements. Utilization of the ideal soft lattice gas model described below leads to the same formalism as that of Darken and interdiffusion coefficients of the system can be obtained as a function of composition.⁵⁴ If the interdiffusion coefficients are the function of composition only and not of the location as in the present case, it can be proved that the Boltzmann's scaling law holds and thus the diffusion paths become time independent. These can thus be calculated analytically.

The fact that unique diffusion paths can exist allows us to analyze thermodynamical properties of diffusion paths.⁴⁵ Based on experimental evidences, Dayananda concluded that zero flux planes can exist at or near the cross section of the isoactivity line which goes through the terminal composition of the diffusion path and the diffusion path. Although it turned out that this prediction was not thermodynamically exact, thermodynamical features of the zero flux planes could be reliably analyzed based on the atomistic treatment.⁴⁵

In the idealized soft lattice gas model, the annihilation and the creation of lattice sites occur on the respective sides of the reference lattice plane in the crystal, and, hence, the reference lattice plane moves with respect to the laboratory frame toward the direction of the annihilation of lattice sites (due to the annihilation of vacancies to keep the vacancy concentration at the local equilibrium value). This is the Kirkendall effect and this effect can also be calculated analytically from the knowledge of the intrinsic diffusion coefficients.⁵⁷ On the other hand, in the case of the diffusion of metallic ions in oxides, the rigid lattice gas model seems to be more suitable than the soft lattice gas model as discussed in detail in the paper of demixing (Category #9) under oxygen partial pressure gradient.²³ In order to keep the vacancy concentration at the local equilibrium value, vacancy distribution is eventually restored and hence the center of mass does not move during the chemical diffusion process even if the diffusional flows from both sides of the diffusion couple do not compensate. In other words, in a strict rigid lattice gas model, it is proved that the chemical diffusion process takes place without the Kirkendall effect.⁵¹ Indeed, in some oxides, such processes seem to be occurring.

Soft lattice gas model and rigid lattice gas model

In chemical diffusion which occurs in a diffusion couple, because the diffusion rates for different species are different, the center of mass moves with diffusion, and this motion is compensated by the motion of vacancies. One of the key assumptions in theoretical treatments

of the chemical diffusion phenomena via the vacancy mechanism is that the vacancy concentration is always at the local equilibrium value during the diffusion process. In the atomistic treatments, this concept can be justified from the fact that the change of macrovariables such as the concentration is much slower as compared to the rate of the unit process. Therefore, in order for an interdiffusion process to occur freely, an unbalance of vacancy concentration distribution results and hence vacancies are either annihilated or created on the respective sides of the reference lattice plane of diffusion. In other words, the lattice sites are either annihilated or created on the respective sides of the reference lattice plane and, hence, the reference lattice plane moves with respect to the reference plane in the laboratory frame. This is the explanation of the well known Kirkendall effect (Category #13) in terms of the atomistic model and the formalism coincides with the formalism adopted by Darken in his phenomenological treatment of the chemical diffusion process. Because the creation and the annihilation of lattice sites is required, we call this lattice gas model as the soft lattice gas model.^{51,57}

However, the soft lattice gas model is not the only possible model to deal with chemical diffusion processes. Let us take the case of chemical diffusion in typical oxides. In this case, oxygen ions are generally immobile and form a rigid lattice, providing lattice sites for metallic ions and these metallic ions diffuse through vacancies in their respective sublattice. In such a case, the annihilation or the creation of vacancies must cooperate with that of oxygen ions, and hence, it is better to regard the sublattice for metallic ions is also regarded as the rigid lattice.^{51,57} In such a case, the local vacancy concentration is kept at the equilibrium value by jumping back of moving vacancies. Since the rate of the unit process is much faster than the change of macrovariables, the above process is equally acceptable in atomistic treatment of diffusion. However, in such a case, because the center of mass cannot move, the chemical diffusion process in a rigid lattice gas model takes place without the Kirkendall effect. On the other hand, diffusion coefficients with respect to the laboratory frame can be proved to be the same as those in the soft lattice gas model and hence the chemical diffusion phenomenon itself is proved to remain the same. Thus the atomistic treatment of chemical diffusion process can give different view points of chemical diffusion process from traditional ones.

Diffusion in Semiconductors

Characteristics of diffusion in semiconductors having the structure of diamond (Si, Ge) and equivalent GaAs type structures have been a center of interest among people in diffusion and many interesting problems, especially in interdiffusion in artificial superlattices, are known. In order to deal with these problems from a unified point of view, a general treatment of diffusion process in semiconductors has been attempted.

In order to describe the features of diffusion, we started from a model of body centered cubic structure which can be separated into four interpenetrating face centered cubic sublattices. In the diamond structure, two of the four sublattices are occupied and two other face centered

cubic sublattices represent the interstitial lattice sites. Diffusion process by means of the nearest neighbor and the second nearest neighbor jumps are treated by the pair approximation of the PPM. The formulations for pure Si or Ge and with impurities have been completed. One trouble found in dealing with this is that, in order to describe the interstitialcy mechanism or the kick-out mechanism which seem to occur in semiconductors, higher order approximation than the pair approximation, and atomic correlation of up to 3rd neighbor, are required and, hence, a formidable task is expected to deal with all the possible diffusion mechanisms with the same degree of approximation. The interstitialcy mechanism and kick-out mechanism can be treated independently as in phenomenological treatments, but this type of treatment does not give any specific advantage of the atomistic treatment.

Formalism of the PPM as Applied to Transport Problems (Category #5)

In order to extract important conclusions of the PPM as applied to transport problems, it is convenient to review general characteristics of the PPM briefly with respect to how it handles kinetic problems. For this purpose, we divide cases to be treated into two general categories: homogeneous and inhomogeneous. If the system is always to be kept statistically homogeneous, a state at a time instant t to be used in the PPM is defined with state variables (which specify the energy of the system) with a corresponding entropy term specified by the Cluster Variation method (CVM). Hence, the state at t is determined as a point on the free energy surface defined by the CVM. Each consecutive state separated by a short time interval Δt defined by the PPM is connected by the condition of the maximum of the Path Probability function (PPF) as the transition probability. Hence, the resultant kinetic path is defined as a line on the free energy surface. Therefore, as long as the system is homogeneous, the kinetics can be described with the accuracy of the CVM with the transition probability which is strictly prescribed in the PPM.^{28,29} The system is always kept under the isothermal condition and new states are established at each Δt instantly. This indicates that the treatment of the PPM in the t space (kinetic space) corresponds to the mean field approximation, but as long as the system is kept homogeneous, the PPM gives an excellent representation of the kinetics.

In dealing with transport problems, systems include gradients in the state variables and are not homogeneous. However, in the linear range, the flow is represented by the motion of particles in the reference state under equilibrium multiplied by the driving force.

Therefore, in dealing with transport problems by the PPM, the motion of particles in the same equilibrium state, rather than in the state on the free energy surface at each time instant is discussed irrespective of whether it is in the adiabatic, intermediate or isothermal time range. This also means that the equilibrium state the PPM represents is that of the adiabatic state, because this is the state connected to the equilibrium state of the system at $t \leq 0$.

If the nearest neighbor distance jump of particles is assumed for the kinetics process, at the adiabatic stage, only particles at the nearest neighbor of the vacancy can contribute to the change of state. Therefore, the pair approximation rather than higher approximation of the PPM

represents the kinetics at the adiabatic state well. Further, if one considers the assembly of particles of the same species and no interactions among particles is taken into account, the pair approximation of the PPM represents the adiabatic condition exactly as long as the concentration of vacancies is negligibly small.

Because in the PPM the treatment in t -space corresponds to the mean field approximation, it is required to improve the degree of approximation of the treatment in the intermediate range through the isothermal range to that of pair in order to be consistent with the treatment of the adiabatic range. For this purpose, the application of the Bethe concept in this time range is appropriate for the reason stated below.

The original Bethe method is devised to deal with the order-disorder transformation in alloys and is known to correspond to the pair approximation in the CVM on which the PPM is based. Here, the consistency relation in the Bethe method which connects the thermodynamical properties of a small cluster to that of its outside gives a change from the local order to the long range order with distance in the form of the propagation of order. This concept can be extended in the present treatment in t -space as follows. In Fig. 1, we show a relation of the tagged particle which has just jumped out, leaving a vacancy at the center at $t=0$ (adiabatic state) which is derived by the pair approximation of the PPM. The distribution of particles around the vacancy, Q_j , is given by the pair approximation of the PPM. The jump back probability of the tagged particle in competition with the surrounding particles under the equilibrium condition (at the adiabatic state), τ at $t=0$, is thus defined. The change of τ which can then be calculated by the Bethe Method in the form of the propagation of order as t changes from 0 to ∞ . The value of τ at $t \rightarrow \infty$ corresponds to the value of τ in the isothermal state in the pair approximation (the increase of τ with time eventually lead the relaxation motion to the KWW behavior).

The combination of the pair approximation of the PPM and the Bethe method thus treats the relaxation of current analytically from the adiabatic state to the isothermal state with the same rigor. The improvement of the degree of approximation of the PPM from the mean field approximation to the pair approximation by means of the Bethe method has been called the conversion process (Category #5). In the past, the conversion process was used to improve the isothermal value of the relaxation effect such as the correlation factor. The importance of the time dependence of τ has been realized only in the last three years. Our recent progress in dealing with the relaxation behavior all based on this principle. That the degree of approximation of the PPM as applied to transport problems is that of the meanfield does not seem to be a familiar fact even among people in the area of PPM.

Fig. 1. Competition of the tagged particle with particles around the vacancy left behind in its jump back process revealed by the pair approximation of the PPM.

Diffusion in Ordered Alloys (Category #7)

The realization that the degree of approximation of the PPM as applied to transport problems is that of the mean field contributed to a number of progress. The present problem is no exception. Earlier, Kikuchi and Sato derived expressions for the tracer diffusion coefficient in binary ordered systems composed of A and B atoms by means of the pair approximation of the PPM,^{2,6} and showed that the tracer diffusion coefficient of B, D_B , is expressed by means of the harmonic mean of two components, D_{BI} and D_{BII} , as

$$\frac{1}{D_B} = \frac{1}{2} \left[\frac{1}{D_{BI}} + \frac{1}{D_{BII}} \right]$$

where D_{BI} (D_{BII}) may be interpreted as a component of the diffusion coefficient when an B^* (tracer of B) atom jump from I sublattice (from a II into a I) site and the smaller one practically determines D_B . This is a convenient concept and has been widely quoted. However, it has been found that a systematic deviation of the calculated values of tracer correlation factor from those obtained by Monte Carlo simulation method in the disordered region exists, but the agreement has been found to be restored when the long range order develops.

It has been found that this discrepancy is due to the fact that the degree of approximation of the original PPM as applied to transport problems corresponds to that of the mean field approximation, and, hence, that the percolation efficiency (equivalent to the correlation factor) of the system is affected drastically only by the development of the long range order. After the conversion (see the previous paragraph), however, it is shown that the change of short range order is responsible for the change of the percolation efficiency.⁶⁷

Kinetics of Relaxation Process of Hopping Ionic Conduction (Category #17)

The problem is derived from an effort to understand the "universal dynamic response" observed in the dispersion process or the relaxation characteristic in the ionic conductivity in disordered solid electrolytes. In other words, disordered solid electrolytes commonly display the following two empirical relations in ionic conductivity. The first is that the frequency dependent ionic conductivity in a certain range of frequency is represented by Jonscher's power law

$$\sigma(\omega) = \omega^p \quad (0 < p < 1) \quad (1)$$

with p limited between 0 and 1, and second, the relaxation process in the induced current when a constant external field is switched on at $t=0$ in such system in non Debye (non exponential) with the behavior to reach the stationary state represented by the Kohlrausch-Williams-Watts (KWW) stretched exponential function $\Xi(t)$

$$\Xi \approx \exp [-(t/\tau)^\beta] \quad [1-p = \beta, \quad 0 < \beta < 1] \quad (2)$$

Eq. (2) indicates that, if the curve is expressed in the form of $\exp [-t/\tau]$, τ increases with time.

In the hopping process, a particle which jumps out to a nearest neighboring site leaves behind a vacancy in the wake, and there is always a high probability for that particle to jump back into the vacancy left behind. This jump back process thus constitutes the relaxation process, and, hence, the above mentioned problem is reduced to a question of whether this jump back process is exponential with time or not.

At this moment, the current view on this problem is that the KWW relation behavior is an anomaly created by interaction and disorder in the distribution of charge carriers. In other words, the non linear relaxation process is ascribed to a coupling with the relaxation process of the surroundings through interactions with neighbors. A number of theories have been worked out from this point of view using specific models and desired effect has been obtained. In addition, highly sophisticated simulation methods in disordered systems such as glass are being developed to see how the universal dynamic response behavior is connected to these models. However, in order to find out the real origin of the universal dynamic response, it is necessary to develop an analytical treatment based on first principles rather than resorting to phenomenological models.

There is an intrinsic difficulty to carry out the above task. Typically, the relaxation curve can be divided into three time regions; adiabatic, intermediate and isothermal. In order to obtain a reasonable conclusion, the relaxation behavior in these three regions has to be calculated with the same vigor. The adiabatic region and the isothermal region are manageable theoretically. At $t=0$, the reference state is the same equilibrium state as that at $t \leq 0$, and in the isothermal region, the reference state is an equilibrium state and a sophisticated linear response theory can be used. However, in the intermediate region, it is necessary to rely on kinetics, because the reference state is not an equilibrium state.

At this point, discussions given in the section "Formalism of the PPM as Applied to Transport Problems" are highly useful. The PPM, in principle, gives an exponential relaxation curve because, here, the same equilibrium state is assumed as the reference state for the adiabatic, intermediate and the isothermal state. On the other hand, the pair approximation of the PPM represents the adiabatic state well. The Bethe method then leads this adiabatic state to the isothermal state in the pair approximation. Therefore, the combination of the pair approximation of the PPM and the Bethe method can consistently describe the relaxation behavior in the pair approximation.

We decided to limit ourselves to the derivation of flow of a single particle in an assembly rather than that of the assembly, because the treatment of the former is far simpler. The relation of the two is now well known, but as far as the mechanism of the relaxation process is concerned, the former is satisfactory as well.

We treat thus the relaxation problem in a lattice gas in two component systems with a pair wise nearest neighbor interaction among charged particles. For the assembly of particles of the same species in a system with negligible number of vacant site without any interaction among particles, the calculation and the interpretation of the results are quite easy. We realize that, in the jump back process of a single particle in the assembly of particles of the same species (without any interaction) with a single vacant site, it is shown that the existence probability of the vacancy at the site left behind increases with time from the value expected at $t=0$ due to the return of the vacancy after its escape resulting from the exchange of position with particles around the vacancy in competition with the tagged particle. This leads the jump back process to exhibit the KWW behavior. As mentioned earlier, this is an apparent contrast to the current view that the anomaly is "created" by interaction and disorder.

In view of the importance of the problem, a copy of our paper "Universal Dynamic Response in Solid Electrolytes: Formalism of the Path Probability Method as Applied to Transport Problems," by H. Sato, A. Datta, and T. Ishikawa",⁷² which is written as a proceeding of the "International Workshop on Theory and Applications of the Cluster Variation and the Path Probability Method," June 19-22, Testihuacan, Mexico is attached as an Appendix.

Publications Related to Transport Problems

1. "Remarks on Magnetically Dilute Systems," H. Sato, A. Arrott and R. Kikuchi, J. Phys. Chem. Solids, 10 19-34 (1959).
2. "Substitutional Diffusion in an Ordered System," R. Kikuchi and H. Sato, J. Chem. Phys., 51, 161-181 (1969).
3. "Correlation Factor in Substitutional Diffusion in Binary Alloys," R. Kikuchi and H. Sato, J. Chem. Phys., 53, 2702-2713 (1970).
4. "Cation Diffusion and Conductivity in Solid Electrolytes, I," H. Sato and R. Kikuchi, J. Chem. Phys., 55, 677-702 (1971).
5. "Cation Diffusion and Conductivity in Solid Electrolytes, II. Mathematical Analyses," R. Kikuchi and H. Sato, J. Chem. Phys., 55, 702-715 (1971).
6. "Diffusion Coefficient in an Ordered Binary Alloy," R. Kikuchi and H. Sato, J. Chem. Phys., 57, 4962-4979 (1972).
7. "Correlation Factor and Nernst-Einstein Relation in Solid Electrolytes", H. Sato and R. Kikuchi; Extended Abstract. 24th Meeting of the International Society of Electrochemistry on Solid Electrolytes, Ion Transport in Insulating Layers and Their Application, Eindhoven Netherlands, Sept. 10-14, 1973.
8. "Correlation Factor and Nernst-Einstein Relation in Solid Electrolytes," H. Sato and R. Kikuchi, Mass Transport Phenomena in Ceramics, Proc. 9th University Conference on Ceramics, ed. A. R. Cooper and A. H. Heuer, Plenum, pp. 149-154 (1975).
9. "Path Probability Method as Applied to Problems of Superionic Conduction", H. Sato and R. Kikuchi, "Superionic Conductors", Proc. Conf. Superionic conductors at Schenectady, New York, May 1976, ed. G. D. Mahan and W. L. Roth, Plenum Press, New York and London (1976), pp. 142.
10. "Superionic Conductivity and Order-Disorder Transition", R. Kikuchi and H. Sato, Ibid., p. 167.
11. "Theoretical Aspects of Diffusion and Ionic Conduction in Super-Ionic-Conductors in Connection with Ordering Transitions," H. Sato and R. Kikuchi, J. de Physique, 38, C7 159-164 (1977).
12. "Some Theoretical Aspects of Solid Electrolytes," H. Sato in "Solid Electrolytes", Topics in Applied Phys. Vol. 21, ed. S. Geller, (1977) Springer p. 3-39.
13. "Kinetics of Order-Disorder Transformation in Alloys, II," K. Gschwend, H. Sato and R. Kikuchi, J. Chem. Phys., 69, 5006-5019 (1978).
14. "Kinetics of Order-Disorder Transformation in Alloys, III," K. Gschwend, H. Sato, R. Kikuchi, H. Iwasaki and H. Maniwa, J. Chem. Phys., 71, 2844-2862 (1979).
15. "Temperature Dependence of Haven Ratio in Fast Ion Conductors and Correlation Effects." H. Sato and R. Kikuchi, Proc. International Conference on Fast Ion Transport in Solids, Eds. P. Vashishta, J. N. Mundy, and G. K. Shenoy, North Holland (1979), pp. 337-340.
16. "Temperature Dependence of the Haven-Ratio in β -Alumina," H. Sato and K. Gschwend, Phys. Rev., B22, 4626-4631 (1980).
17. "The Haven Ratio and the Percolation Problem in β -Alumina," H. Sato, Proc. International Conference on Fast Ion Transport, 1981 Gatlinburg, Solid State Ionics, 5, 183-186 (1981).

18. "Theory of Many-Body Diffusion by the Path Probability Method: Conversion from the Ensemble Averaging to the Time Averaging," H. Sato and R. Kikuchi, *Phys. Rev. B.*, 28, 648-664 (1983).
19. "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).
20. "Statistical Mechanics of Thermal Diffusion," R. Kikuchi, T. Ishikawa and H. Sato, *Physica* 123A 227-252 (1984).
21. "Ionic Conductivity in Binary Systems", A. Suzuki, H. Sato and R. Kikuchi, *Phys. Rev. B*29, 3550-3566 (1984).
22. "The Application of the Path Probability Method to Transport Phenomena," H. Sato, *Nontraditional Methods in Diffusion*, edited by G. E. Murch, H. K. Birnbaum and J. R. Cost, TMS-AIME Conference Proceedings Volume, (1984), pp. 203-235.
23. "Demixing of Materials under Chemical Potential Gradients," T. Ishikawa, H. Sato, R. Kikuchi and S. A. Akbar, *J. Am. Cer. Soc.*, 68, 1-6 (1985).
24. "Soret Effect in Solids," K. Wada, A. Suzuki, H. Sato and R. Kikuchi, *J. Phys. Chem. Solids*, 46, 1195-1205 (1985).
25. "Correlation Factor in Tracer Diffusion for High Tracer Concentrations," H. Sato, T. Ishikawa and R. Kikuchi, *J. Phys. Chem. Solids.*, 46, 1361-1370 (1985).
26. "Tracer Diffusion in an Ordered Alloys: Application of the Path Probability and Monte Carlo Methods," H. Sato, S. A. Akbar and G. E. Murch, *Diffusion in Solids: Recent Developments*, edited by M. A. Dayananda and G. E. Murch, TMS-AIME Conference Proceedings Volume (1985), pp. 67-95.
27. "Percolation Efficiency and Mixed Alkali Effect," H. Sato, K. Wada, A. Suzuki and S. A. Akbar, *Solid State Ionics*, 18-19, 178-182 (1986).
28. "Time Evolution of Fluctuations in the Path Probability Method I," T. Ishikawa, K. Wada, H. Sato and R. Kikuchi, *Phys. Rev. A.*, 33, No. 6, 4164-4170 (1986).
29. "Time Evolution of Fluctuations in the Path Probability Method II," K. Wada, T. Ishikawa, H. Sato and R. Kikuchi, *Phys. Rev. A.*, 33, No. 6, 4170-4178 (1986).
30. "Theory of Hopping Conduction by the Path Probability Method," T. Ishii, H. Sato and R. Kikuchi, *Phys. Rev. B.* B34, 8335-8344 (1986).
31. "Demixing of Oxides under a Temperature Gradient," S. A. Akbar, M. Kaburagi, H. Sato and R. Kikuchi, *J. Am. Cer. Soc.* 70, [4] 246-253 (1987).
32. "Soret Effect in Solid, II," S. A. Akbar, M. Kaburagi and H. Sato, *J. Phys. Chem. Solid.* 48, 579-586 (1987).
33. "Atomic Transport under the Coexistence of Temperature and Oxygen Potential Gradient," S. A. Akbar and H. Sato, *N. L. Peterson Memorial Symposium on Oxidation of Metals and Associated Mass Transport*, edited by M. A. Dayananda, S. Rothman and W. E. King, TMS-AIME Conference Proceedings Volume (1987) pp. 49-65.
34. "Time Evolution of Demixing in Oxides under Oxygen Potential Gradient," T. Ishikawa, S. A. Akbar, W. Zhu and H. Sato, *J. Am. Cer. Soc.*, 71, (7), 513-521 (1988).
35. "Frequency Dependence of Ionic Conductivity as Treated by the Path Probability Method," T. Ishii, H. Sato and R. Kikuchi, *Solid State Ionics*, 28-30, 108-114 (1988).
36. "Frequency Dependence of Hopping Ionic Conductivity and Mixed Alkali Effect," H. Sato, S. A. Akbar and T. Ishii, *Solid State Ionics*, 28-30, 138-141 (1988).

37. "Diffusion in Multicomponent System under Stress Gradient," M. Kaburagi, H. Sato and R. Kikuchi, Proceedings of JIMIS-5: Non Equilibrium Solid Phases of Metals and Alloys, Suppl. Trans. JIM, 29 199-202 (1989).
38. "Chemical Diffusion in Alloys," T. Ishikawa, H. Sato, R. Kikuchi, A. S. Akbar, W. Zhu and A. S. Datta, Metallurgical Transaction of AIME.
39. "Demixing: A Source of Material Deterioration," S. A. Akbar and H. Sato, J. Phys. Chem. Solids, 50 [No. 7] 729-733 (1989).
40. "Phenomenological Theory for Superionic Transport," T. Ishikawa and H. Sato in "Superionic Solids and Solid Electrolytes: Recent Trends," eds. A. L. Laskar and S. Chandra, Academic Press, (1989) pp. 439-471.
41. "Atomistic Treatment of Chemical Diffusion in Multicomponent Alloys: Theoretical Analysis of "Zero-Flux Planes," H. Sato, Diffusion Analysis and Applications, edited by A. D. Romig, Jr., and M. A. Dayananda, The Minerals, Metals and Materials Society (1989) pp. 19-33.
42. "Diffusion in Multicomponent System under Stress Gradient," M. Kaburagi, H. Sato and R. Kikuchi, Proceedings of JIMIS-5: Non Equilibrium Solid Phases of Metals and Alloys, Suppl. Trans. JIM, 29 199-202 (1989).
43. "Demixing: A Source of Material Deterioration," S. A. Akbar and H. Sato, J. Phys. Chem. Solids, 50 [No. 7] 729-733 (1989).
44. "Phenomenological Theory for Superionic transport," T. Ishikawa and H. Sato in "Superionic Solids and Solid Electrolytes: Recent Trends," eds. A. L. Laskar and S. Chandra, Academic Press (1989), pp. 439-471.
45. "Atomistic Treatment of Chemical Diffusion in Multicomponent Alloys: Theoretical Analysis of Zero-Flux Planes," H. Sato, Diffusion Analysis and Applications, edited by A. D. Romig, Jr., and M. A. Dayananda, The Minerals, Metals and Materials Society (1989), pp. 19-33.
46. "Theoretical Background for the Mixed Alkali Effect," H. Sato, Solid State Ionics, 40/41, 725-733 (1990).
47. "Atomistic Approach of Chemical Diffusion Phenomena," H. Sato and R. Kikuchi, "Fundamentals and Applications of Ternary Diffusion," Proceedings of the International Symposium, ed. G. R. Purdy, Proceedings Vol. 23, The Metallurgical Society of the Canadian Institute of Mining and Metallurgy, Pergamon Press (1990), pp. 15-22.
48. "Percolation Threshold for Electronic Conduction in β -Alumina Type Compounds," M. Sankararaman, R. Kikuchi and H. Sato, Journal of Solid State Chemistry, 88 [No. 1] 239-246 (1990).
49. "Theoretical Background for the Mixed Alkali Effect," H. Sato, Solid State Ionics, 40/41, 725-733 (1990).
50. "Percolation Threshold for Electronic Conduction in β -Alumina Type Compounds," M. Sankararaman, R. Kikuchi and H. Sato, Journal of Solid State Chemistry, 88 [No. 1] 239-246 (1990). #2
51. "Atomistic Approach of Chemical Diffusion Phenomena," H. Sato and R. Kikuchi. "Fundamentals and Applications of Ternary Diffusion," Proceedings of the International Symposium, ed. G. R. Purdy, Proceedings Vol. 23, The Metallurgical Society of the Canadian Institute of Mining and Metallurgy, Pergamon Press (1990), pp. 15-22. #3
52. "Atomistic Approach of Chemical Diffusion Phenomena," H. Sato and R. Kikuchi. "Fundamentals and Applications of Ternary Diffusion," Proceedings of the International Symposium, ed. G. R. Purdy, Proceedings Vol. 23, The Metallurgical Society of the

- Canadian Institute of Mining and Metallurgy, Pergamon Press (1990), pp. 15-22.
53. "Atomistic Treatment of Chemical Diffusion in Multicomponent Alloys: Relation between Intrinsic Diffusion Coefficients and Diffusion Coefficients in the Laboratory Frame," H. Zhang, A. Datta and H. Sato, "Atomic Migration and Defects in Materials," eds. D. Gupta, H. Jain and R. W. Siegel, Sci-Tech Publication (1991), pp. 107-114.
 54. "Atomistic Treatment of Chemical Diffusion Phenomena in Oxides and in Metallic Alloys," H. Sato and A. Datta, Atomic Migration and Defects in Materials, eds. D. Gupta, H. Jain and R. W. Siegel, Sci-Tech Publication (1991), pp. 115-120.
 55. "Theoretical Aspects of Mixed Alkali Effect," H. Sato, Ceramic Transactions, Vol. 20, Glasses for Electronic Applications, Ed. K. M. Nair, The American Ceramic society (1991), pp. 19-39.
 56. "Atomistic Treatment of Chemical Diffusion in Multicomponent Alloys: Relation between Intrinsic Diffusion Coefficients and Diffusion Coefficients in the Laboratory Frame," H. Zhang, A. Datta and H. Sato, "Atomic Migration and Defects in Materials," eds. D. Gupta, H. Jain and R. W. Siegel, Sci-Tech Publication (1991), pp. 107-114.
 57. "Atomistic Treatment of Chemical Diffusion Phenomena in Oxides and in Metallic Alloys," H. Sato and A. Datta, Atomic Migration and Defects in Materials, eds. D. Gupta, H. Jain and R. W. Siegel, Sci-Tech Publication (1991), pp. 115-120.
 58. "Theoretical Aspects of Mixed Alkali Effect," H. Sato, Ceramic Transactions, Vol. 20, Glasses for Electronic Applications, Ed. K. M. Nair, The American Ceramic society (1991), pp. 19-39.
 59. "Path Probability Method of Irreversible Statistical Mechanics: An Overview," H. Sato, Materials Transactions, JIM, 32 (1991) 509-525.
 60. "Theoretical Aspects of Mixed Alkali Effect," H. Sato, Ceramic Transactions, Vol. 20, Glasses for Electronic Applications, Ed. K. M. Nair, The American Ceramic Society (1991), pp. 19-39.
 61. "Frequency Dependence of Ionic Conductivity in Interacting Lattice Gas Systems," H. Sato, T. Ishikawa and K. Funke, Solid State Ionics, 53-56 (1992) 907.
 62. "Percolation Threshold for Electronic Conduction in β -Alumina Type Compounds, II," A. Datta, R. Kikuchi and H. Sato, Solid State Ionics, 53-56 (1992) 453.
 63. "Atomistic Approach of Chemical Diffusion," H. Sato and Huanbo Zhang, Defect and Diffusion Forum (Proceedings, DIMAT-92), Defect and Diffusion Forum 95-98 (1993) 37.
 64. "Time Dependent Correlation Factor," H. Sato and A. Datta, Defect and Diffusion Forum (Proceedings, DIMAT-92), Defect and Diffusion Forum 95-99 (1993) 57.
 65. "Examination of Local Equilibrium Concept in Diffusion," H. Sato, Defect and Diffusion Forum (Proceedings, DIMAT-92), Defect and Diffusion Forum 95-98 (1993) 713.
 66. Non-Debye Relaxation Process of Hopping Ionic Conduction in Lattice Gas Models, H. Sato and A. Datta, Solid State Ionics III, edited by B.-A. Nazri, J.-M. Tarascon and M. Armand, Mat. Res. Soc. Symp. Proc. Vol. 293 (1993), Materials Research Society, pp. 213-218.
 67. "Atomistic Approach to Diffusion in Ordered Alloys," H. Sato and H. Zhang, "Diffusion in Ordered Alloys," edited by B. Fultz, R. W. Cahn and D. Gupta, The Minerals, Metals and Materials Society, pp. 21-32 (1993).
 68. "Non Debye Relaxation Process of Hopping Ionic Conduction in Lattice Gas Models: An Application of the Path Probability Method," H. Sato, Progress Theor. Phys. Suppl. 15

- (1994) 317.
69. "Frequency Dependence of Ionic Conductivity in Lattice Gas Models," Hiroshi Sato and Anuradha Datta, *Solid State Ionics*, 72 19 (1994).
 70. Non Debye Relaxation Process in Hopping Ionic Conduction, Hiroshi Sato, *Ionic and Mixed Conducting Ceramics*, Second International Symposium, Edited by T. A. Ramanarayanan, W. L. Worrell and H. L. Teller, Electrochemical Society, Inc., *Proceedings Vol. 94-12*, pp. 552-562 (1994).
 71. "Relaxation Process of Hopping Ionic Conduction Lattice Gas Models," Hiroshi Sato, Anuradha Datta and Takuma Ishikawa, *Proc. International Workshop on Solid State Ionics*, Tokyo (Nov. 1994), *Solid State Ionics*, to be published.
 72. Universal Dynamic Response in Solid Electrolytes: Formalism of the Path Probability Method as Applied to Transport Problem, Hiroshi Sato, Anuradha Datta and Takuma Ishikawa, *Proc. International Workshop on Theory and Applications of the Cluster Variation and the Path Probability Method*, June (1995), to be published.
 73. Kinetics of Relaxation Process of Hopping Ionic Conduction in Lattice Gas Models, Hiroshi Sato, Anuradha Datta and Takuma Ishikawa, *J. Noncrystalline Solids (Proc. 13th University Conference on Glass Science)*, Aug. 9-11 (1995), to be published.
 74. Kinetics of the Relaxation Process of Hopping Ionic Conduction in Lattice Gas Models, Hiroshi Sato, Anuradha Datta and Takuma Ishikawa, *Proceeding of Solid State Ionics 10*, Dec. 3-8 (1995), to be published in *J. Solid State Ionics* (1996).

**Universal Dynamic Response in Solid Electrolytes:
Formalism of the Path Probability Method as Applied to Transport Problems**

Hiroshi Sato, Anuradha Datta and Takuma Ishikawa*

School of Materials Engineering, Purdue University

W. Lafayette, IN 47907-1289, USA

Abstract

The relaxation process of hopping ionic conduction in interacting lattice gas systems has been treated analytically from first principles in order to gain understanding of the origin of the "universal dynamic response" in solid electrolytes. The derivation is based on the combination of the pair approximation of the Path Probability Method and the Bethe method. The result indicates that the relaxation motion of a single particle in a lattice gas is intrinsically non Debye and follows the Kohlrausch-Williams-Watts relaxation behavior even without any interactions among mobile particles. This conclusion is in apparent contrast to the current view that the anomaly is created by interaction among mobile particles and their disorder. It can be shown that the appearance of the KWW effect is due to a memory effect arising from the fact that it takes time for information to propagate over a distance by hopping which has been overlooked so far. A Monte Carlo simulation of the relaxation process was made and the results support the above concept.

*Faculty of Engineering, Tokyo Institute of Polytechnics, Atsugi, Kanagawa 243-02, Japan.

1. Introduction

The major interest of this treatment is to understand the "universal dynamic response" observed in the dispersion process or the relaxation characteristics in the ionic conductivity in solid electrolytes, and to examine the formalism of the Path Probability Method (PPM) as applied to transport problems at the same time.

The phenomenon "universal dynamic response" is generally represented by the following two empirical relations [1,2]; the first indicates that the frequency dependent ionic conductivity $\sigma(\omega)$ is represented by the Jonscher's power law

$$\sigma(\omega) \equiv \omega^p \quad (0 < p < 1) \quad (1)$$

with p limited between 0 and 1, and, the second, the relaxation process in the induced current when a constant external field is switched on at $t=0$ in such systems is non Debye (non exponential) with the behavior to reach the stationary state represented by the Kohlrausch-Williams-Watts (KWW) stretched exponential function $\Xi(t)$ [2]

$$\Xi(t) \approx \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \quad (1 - p = \beta, 0 < \beta < 1) \quad (2)$$

Eq. (2) indicates that, in the expression of the form $\exp [-(t/\tau)]$, τ increases with time.

In the hopping process, a particle which jumps out to a nearest neighboring vacancy leaves behind a vacancy in its wake, and there is always a high probability for that particle to jump back into the vacancy which had been left behind. This jump back process thus constitutes the relaxation process in the hopping motion and, hence, the problem is reduced to the question of whether this jump back process is exponential with time or not.

The task involved here is to derive the relaxation curve for the induced current upon the application of a constant external field at $t=0$ in the lattice gas model. Here, we limit ourselves to the derivation of flow of a single particle in an assembly rather than that of the assembly, because the treatment of the former is far simpler. The relation between the two is now well known [3],

but, as far as the mechanism of the relaxation process is concerned, the former is satisfactory as well.

Typically, the relaxation curve can be divided into three time regions: adiabatic, intermediate and isothermal [4] as shown in Fig. 1. If the relaxation curve is normalized, the curve represents the time dependent correlation factor $f(t)$ as introduced by Funke [2] and the relaxed value in the isothermal region for flow of a single particle is commonly called the tracer correlation factor. The difficulty in deriving the relaxation behavior theoretically is to deal with all the three time regions with equal rigor. The adiabatic region and the isothermal region are manageable because at $t \leq 0$, the system is in equilibrium up to the adiabatic state and, in the isothermal region, a highly sophisticated linear response theory can be used. However, in the intermediate region, it is necessary to rely on kinetics, because the reference state is not the same equilibrium state. If the same equilibrium state persists from the adiabatic range through the isothermal range, the jump back process should be exponential, because this reduces the relaxation process to the Markovian process [5]. Therefore, prior theoretical efforts emphasize that the KWW effect should arise from interactions among mobile particles and their disordered arrangements [6]. This means that the origin of the nonlinear relaxation process is ascribed to a coupling with the relaxation process of the surroundings through interactions with neighbors. Several phenomenological theories have been developed for the appearance of the KWW behavior by constructing models to account for the difference in the equilibrium state in the adiabatic range and in the isothermal range [2,7,8]. For this, the models require interactions among mobile ions and their disordered arrangements. Also, highly sophisticated simulation models in disordered systems such as glass are being developed to account for the universal dynamic response. However, in order to understand the real origin of the universal response, it is necessary to develop an analytical treatment based on first principles rather than resorting to phenomenological models.

We have developed such an analytical theory for interacting lattice gas models by combining the pair approximation of the Path Probability Method (PPM) and the Bethe method. Here, the PPM is utilized to describe the adiabatic state correctly while the Bethe method is used to

lead this adiabatic state to the isothermal state correctly through the intermediate state in the form of the propagation of order. The background of why the relaxation process can be analytically described with the pair approximation from the adiabatic state to the isothermal state will be given briefly. By applying this treatment to the jump back process of the tagged particle in the assembly of particles of the same species (without any interaction) with a single vacant site, we realize that the existence probability of the vacancy at the left behind site increases with time from the value expected at $t = 0$ due to its return after the escape. This leads the jump back process to the KWW behavior. In these treatments, the result for a one dimensional lattice is confirmed to be exact. A Monte Carlo simulation of the time dependent correlation factor is made for the assemblies of particles of the same species. The agreement with analytical calculations is found to be excellent.

The behavior which represents the universal dynamic response is thus extracted from the analytical results.

2. Formalism of the PPM

In order to extract important conclusions of the PPM as applied to transport problems, it is convenient to review general characteristics of the PPM briefly with respect to how it handles the kinetic problems. For this purpose, we divide cases to be treated into two general categories; homogeneous and inhomogeneous. If the system is to be kept always statistically homogeneous, a state at a time instant t to be used in the PPM is defined with state variables (which specify the energy of the system) with a corresponding entropy term specified by the Cluster Variation method (CVM). Hence, the state at t is determined as a point on the free energy surface defined by the CVM. Each consecutive state separated by a short time interval Δt defined by the PPM is connected by the condition of the maximum of the Path Probability function (PPF) as the transition probability. Hence, the resultant kinetic path is defined as a line on the free energy surface. Therefore, as long as the system is homogeneous, the kinetics can be described with the accuracy of the CVM with the transition probability which is strictly prescribed in the PPM [9,10]. The system is always kept under the isothermal condition and new states are established at each Δt

instantly. This indicates that the treatment of the PPM in the t space (kinetic space) corresponds to the mean field approximation, but as long as the system is kept homogeneous, the PPM gives an excellent representation of the kinetics.

In dealing with transport problems, systems include gradients in the state variables and are not homogeneous. However, in the linear range, the flow is represented by the motion of particles in the reference state under equilibrium multiplied by the driving force. Therefore, in dealing with transport problems by the PPM, the motion of particles in the same equilibrium state, rather than in the state on the free energy surface at each time instant is discussed irrespective of whether it is in the adiabatic, intermediate or isothermal time range. This also means that the equilibrium state which the PPM represents is that of the adiabatic state, because this is the state connected to the equilibrium state of the system at $t \leq 0$.

If the nearest neighbor distance jump of particles is assumed for the kinetic process, at the adiabatic stage, only particles at the nearest neighbor of the vacancy can contribute to the change of state. Therefore, the pair approximation rather than higher approximation of the PPM represents the kinetics at the adiabatic state well. Further, if one considers the assembly of particles of the same species and no interactions among particles is taken into account, the pair approximation of the PPM represents the adiabatic condition exactly as long as the concentration of vacancies is negligibly small.

Because the PPM corresponds to the mean field approximation in t -space, it is required to improve the degree of approximation in t -space to that of pair in order to be consistent with the treatment of the adiabatic state. For this purpose, the application of the Bethe concept is appropriate for the reason stated below.

The original Bethe method [11] is devised to deal with the order-disorder transformation in alloys and is known to correspond to the pair approximation in the CVM on which the PPM is based. Here, the consistency relation [11] in the Bethe method which connects the thermodynamical properties of a small cluster to that of its outside gives a change from the local order to the long range order with distance in the form of the propagation of order [12]. This

concept can be extended in the present treatment in t -space as follows. In Fig. 2, we show a relation of the tagged particle which has just jumped out, leaving a vacancy at the center at $t=0$ (adiabatic state) which is derived by the pair approximation of the PPM. The distribution of particles around the vacancy, Q_j , is given by the pair approximation of the PPM. The jump back probability of the tagged particle in competition with the surrounding particles under the equilibrium condition (at the adiabatic state), τ at $t=0$, is thus defined. The change of τ with t can then be calculated by the Bethe Method in the form of the propagation of order as t changes from 0 to ∞ . The value of τ at $t \rightarrow \infty$ corresponds to the value of τ in the isothermal state in the pair approximation.

The combination of the pair approximation of the PPM and the Bethe method thus treats the relaxation of current analytically from the adiabatic state to the isothermal state with the same rigor.

3. Formal Treatment of the Relaxation Process by the PPM

Here, we deal with the calculation of the relaxation of flow when a constant driving force for the tagged particle, $\dot{\alpha}_i$, is switched on at $t=0$ in a binary system consisting of A and B (and of tracer particle of B or B*) indicated by i and j which specify A, B and B* as 1, 2 and 3, respectively in a lattice gas with pairwise, nearest neighbor interactions, ϵ_{AA} , ϵ_{BB} and $\epsilon_{AB} = \epsilon_{BA}$ among mobile particles A and B by means of the pair approximation of the PPM. A detailed derivation of the tracer correlation factor in the range $t \rightarrow \infty$ has been carried out and is shown in the Appendix of reference [13].

The flow equation for a small number of tracer ions in the disordered distribution in the linear approximation at a time instant t is written down as

$$\Psi_i(t) = -\dot{\alpha}_i + \sum_{j=1}^3 Q_j \Psi_{ji}(t) \quad (j = 1, 2 \text{ and } 3, \quad j = 1, 2 \text{ and } 3) \quad (3)$$

Here, i is meant to be the tagged species. Therefore, Ψ_i indicates the normalized flow at t of the tagged species, Q_j specifies the equilibrium distribution of particles represented by the concentration of the j th species around the vacancy, $\Psi_{ji}(t)$ indicates the gradient in the distribution of particles created by the driving force for the i th species $\dot{\alpha}_i$. $\Psi_i(t)$ is evaluated in a short time period between t and $t+\Delta t$ under the same reference state under equilibrium Q_j at any t .

Based on Eq. (3), we can rewrite

$$\begin{aligned}\Psi_i(t) &= -f_i(t) \cdot \dot{\alpha}_i \\ &= -\left(1 - \sum_{j=1}^3 Q_j \Psi_{ji}/\dot{\alpha}_i\right) \cdot \dot{\alpha}_i\end{aligned}\quad (4)$$

This defines the time dependent correlation factor. In this expression, the first term represents the jumping out of the tagged particle from the central site (at $t=0$) in Fig. 2 and the second term represents the jumping back of the tagged particle into the vacancy. Here, the time dependent correlation factor takes the form of $1-A_i(t)$ as in Eq. (4) and $A_i(t)$ takes the form of an exponential function because $\Psi_{ji}(t)$ in Eq. (3) is a function of t only. In other words, in the disordered state, the relaxation process is expressed by the PPM in terms of a single exponential mode even in binary systems. Our major interest is to examine $1-A_i(t)$ with the aid of the Bethe method through the use of τ_i .

If mutual interactions among mobile ions are taken into account, there should be four independent state variables (even if the distribution of vacancies is considered to be random) and there should then be four relaxation modes (in case the long range order exists) in the binary alloys [14,15]. In such a case, the time dependent correlation factor should be composed of four exponential modes and, hence, the relaxation mode becomes non Debye even in the mean field approximation. However, our concern here is to show that each relaxation mode thus defined is non Debye. The result that, in the disordered state, the number of mode is reduced to one is due to the fact that the PPM is a mean field approximation in t -space [16].

Equation (3) can be most easily handled in the time region $t \rightarrow \infty$ where $\psi_{ij}(t)$ saturates and does not change with time [13]. In this time region, the stationary state value of Ψ_i can be solved in terms of a time independent function Z_i as

$$\Psi_i = - \{ [(2\tilde{\omega}-1)Z_i] / [2 + (2\tilde{\omega}-3)Z_i] \} \cdot \dot{\alpha}_i \quad (5)$$

where Z_i represents

$$Z_i = \sum_j (Q_j \hat{w}_j) / (\hat{w}_i + \hat{w}_j) \quad (6)$$

and $2\tilde{\omega}$ represents the coordination number. In Eq. (6), $\hat{w}_j$, etc. are defined as the jump frequency of the j th species including the bond breaking factor. The meaning of Z_i is clear from Fig. 2 which represents the second term of Eq. (3) and the jump back probability of the tagged particle into the vacancy left behind in competition with other particles around the vacancy under the equilibrium condition is being calculated. Here, the quantity $1-Z_i$ represents the jump back (return) probability P_r of the tagged particle whereas Z_i represents the escape probability P_e (the jumping-in probability of a particle other than the tagged particle). The normalized jump back probability is then defined as

$$\tau_i = (1-Z_i) / [(1-Z_i) + (2\tilde{\omega}-1)Z_i] \quad (7)$$

It should be realized that τ_i in Eq. (7) means not only a normalized jump back probability of a particle of the i th species under equilibrium, but also the jump back probability of the tagged particle (the i th species) at $t=t_0$ (defined as $\tau_i^*(t_0)$) in the time range $t \rightarrow \infty$. In terms of $\tau_i = \tau_i^*(t_0)$, the tracer correlation factor f_i (at t_0) is defined as

$$f_i = (1-\tau_i)/(1+\tau_i) \quad (8)$$

Since the time dependence of the reference state is dealt with, and since τ_i depends on the reference state, τ_i is indirectly time dependent. However, here, the expression such as $\tau(t)$ is avoided in order not to confuse with the explicit time dependence of $\tau_i^*(t)$. Equation (3) has the same form at any t except for the value of $\psi_{ji}(t)$. Because of this, at any t , the same type of solution for $\tau_i^*(t)$ should exist. Then, the time dependent correlation factor for the i th species $f_i^*(t)$ is determined from the relation

$$f_i^*(t) = \frac{1 - \tau_i^*(t)}{1 + \tau_i^*(t)} \quad (9)$$

as long as $\tau_i^*(t)$ can be obtained (we put an asterisk to $f_i(t)$ in order to conform to the previous treatment) rather than as $1 - A_i(t)$. With the aid of Fig. 2 and Eq. (7), $\tau_i^*(t)$ can be obtained as

$$\tau_i^*(t) = \tau_i (1 - e^{-\frac{\dot{w}_i}{\tau_i} t}) \quad (10)$$

Here, $\tau_i^*(t)$ tends to τ_i as $t \rightarrow \infty$ as expected.

In the PPM, the background equilibrium state is the same from the adiabatic state to the isothermal state and, hence, τ_i remains the same. Therefore, in the PPM, the relaxation of $\tau_i^*(t)$ is exponential. However, if the reference state changes from the adiabatic state to the isothermal state and τ increases with time, the relaxation of $\tau_i^*(t)$ becomes KWW, and so does $f^*(t)$. The essential part of the present work is to investigate the dependence of τ_i with t from the adiabatic state to the isothermal state by means of the Bethe method.

The treatment of the PPM combined with the Bethe method is equivalent to the assumption of a "stochastic model" for the jump of constituent particles in the lattice gas model. We observe the system and when a particle exchanges with a vacancy, we set $t=0$ and tag the particle, and the

correlation of the tagged particle with the vacancy is closely followed from $t=0$ to $t \rightarrow \infty$. The whole system is kept under the equilibrium condition.

4. Conversion of the Averaging Process

In the PPM, the flow of the tagged particle is calculated at each time instant (separated by Δt) in the reference state under equilibrium in competition with particles around the vacancy with the averaged distribution Q_j and with its (averaged) jump frequency $\hat{w}_j$ specified by the Cluster Variation method (CVM). In this respect, in Eq. (3), the values of Q_j and $\hat{w}_j$ do not fluctuate with time and takes the same averaged values (ensemble average) at any time. In other words, in the original PPM, a flow in a binary system is treated as a flow in a homogeneous system consisting of averaged particles with averaged jump frequencies. In reality, the distribution of surrounding particles, Q_j , cannot remain the same, but should fluctuate from time to time between two values which represent the short range order distribution Q_j^α around an A particle and Q_j^β around a B particle, respectively, which is specified by the pair approximation of the CVM (instantaneous distribution conversion process) [17-18]. At the same time, the jump frequency of a particle at the surrounding of the vacancy left behind is not that of the averaged particle $Q_j \hat{w}_j$, but should fluctuate between that of an A particle and of a B particle with time (time conversion process) [13,17,18]. Since the system as a whole is kept under equilibrium, the ensemble average is the same as the time averaging and the fluctuation is allowed within this limit. In other words,

1. Instantaneous Distribution Conversion Process

$$Q_j \rightarrow x_A Q_j^\alpha + x_B Q_j^\beta \quad (11)$$

2. Time Conversion Process

$$Q_j \hat{w}_j (1 - \tau_j) \rightarrow Q_A \hat{w}_A (1 - \tau_A) + Q_B \hat{w}_B (1 - \tau_B) \quad (12)$$

The inclusion of the factor $(1-\tau_j)$, etc. in Eq. (12) indicates that particles on the average are moving with a jump back probability τ_j as specified in the Bethe method [11].

With the instantaneous distribution conversion process, the number of mode in the disordered binary alloys increases from one to four according to the number of independent state variables [16]. Based on Eq. (11), we eventually deal with two types of flow each for A and B particles with specific surroundings Q_j^α and Q_j^β in converting to the Bethe method. This conversion can be handled by the concept of microscopic balance [16]. In this paper, however, we do not proceed further on this concept.

5. Assembly of Particles of the Same Species with a Negligible Amount of Vacancies

Here, we treat the problem of a motion of a single particle in the assembly of particles of the same species without any mutual interaction with a negligible amount of vacant sites in a lattice gas. Without any interactions among mobile particles, and with no species of particles to be distinguished, the pair approximation of the PPM represents the exact adiabatic condition.

From Eq. (6) of the pair approximation of the PPM, without the need of specifying the tagged species

$$Z = w/(w + w) \quad (13)$$

where w represents the jump frequency of the particle. From this, the adiabatic value of τ is obtained using Eq. (7) as $\tau = w/\{w + (2\bar{\omega}-1)w\}$. For $t \geq 0$, utilizing the time conversion relation Eq. (12)

$$Z = [w(1-\tau)] / [w + w(1-\tau)] = (1-\tau)/(2-\tau) \quad (14)$$

The consistency relation in τ is then obtained with the use of Eq. (7)

$$\tau = 1/[2\bar{\omega} - (2\bar{\omega} - 1)\tau] \quad (15)$$

in the form of an iteration formula. Eq. (15) can be written in a differential form as

$$\frac{d\tau}{dN} = \frac{2[2\bar{\omega} - (2\bar{\omega} - 1)\tau][1 - (2\bar{\omega} - 1)\tau][1 - \tau]}{(2\bar{\omega} - 1) + [2\bar{\omega} - (2\bar{\omega} - 1)\tau]^2} \quad (16)$$

where N represents the number of iterations. As the number of iterations, N , increases, τ approaches the isothermal value $\tau \rightarrow 1/(2\bar{\omega} - 1)$ ($N \rightarrow \infty$) from the adiabatic value $\tau = 1/(2\bar{\omega})$ ($N=1$) in Eq. (15). Therefore, if N is related to time t , Eq. (16) represents the propagation of order, $d\tau/dt$, in t space through $d\tau/dN$.

The number of iterations N represents the distance of propagation of information, and, hence, represents the number of jumps n which effectively covers N unit distance by the vacancy which makes a random walk. If so, N and the number of jumps n are related as $N = \sqrt{n}$ and $t = n/w$. Because $N=1$ corresponds to $t=0$, $N-1 = \sqrt{wt}$ [19]. This is the relation between N and t . The propagation of order in Eq. (15) means that information at the center of the group in Fig. 2 is accumulated over a distance with time by hopping of particles [20] represented by the motion of vacancy. Here, specifically, the increase of τ indicated in Fig. 3 represents the return of the escaped vacancy with time. The presence of interactions among conduction ions, especially those which tend to create an ordering of conduction ions enhances the KWW behavior.

In Fig. 3, τ - t relations are plotted for different values of $2\bar{\omega}$ with $2\bar{\omega} = 2$ for the one dimensional lattice, 3 for the two dimensional honeycomb lattice, 4 for the two dimensional square net and 8 for the body-centered cubic lattice. The increase of τ with t means that $\tau^*(t)$ and, hence, $f^*(t)$ also have the KWW behavior (Eq. (10)). In other words, the non Debye behavior is inherent even in the single mode case although the effect is almost negligible except for the case, $2\bar{\omega} = 2$.

Based on Eq. (16), the increase of τ as $t \rightarrow \infty$ for cases with $2\bar{\omega} > 2$ is exponential, but for the one dimensional case ($2\bar{\omega} = 2$), where the percolation limit is reached as $t \rightarrow \infty$, the decay becomes proportional to $t^{-1/2}$. The change of the rate of approach from exponential to $t^{-1/2}$ is observed in Fig. 4 which shows $d(\log f^*(t))/d(\log t)$ at the value $f^*(t)$ around 0.1. The extensive linearity in the relation $\log f(t) - \log t$ such as that observed for the case $2\bar{\omega} = 2$ is also observed in systems where $f(t)$ decreases with time to a small enough value such as in mixed alkali systems [21]. This is due to the existence of a scaling law for the decrease of $f(t)$ with time near the percolation limit. The value of p is obtained from the slope of this curve as $d(\log f(t))/d(\log t) = -p$ and are 0.12, 0.22, 0.32 and 0.5, respectively for $2\bar{\omega} = 6, 4, 3$ and 2. The value 0.5 for the one dimensional lattice is proven to be the exact value for this case. The relation $\log f^*(t) - \log t$ can be converted to $\log f^*(\omega) - \log \omega$ by simply converting t into $2\pi/\omega$. The Jonscher's power law exponent, p , can be obtained from $d(\log f^*(\omega))/d(\log \omega) = p$, too.

As mentioned earlier, Monte-Carlo simulation of the relaxation process can be made in a straightforward fashion. The simulation calculates $f^*(t) = - \int_0^t \langle v(0)v(t') \rangle / \langle v^2(0) \rangle dt'$ directly, assuming a single vacancy in the system which makes the random walk starting from an instant when the vacancy has exchanged places with the tagged particle. The agreement of the analytical calculation of $f^*(t)$ obtained from $\tau^*(t)$ (Eq. (11)) with the Monte-Carlo simulation of $f^*(t)$ is excellent. In the case $2\bar{\omega} = 3$, where the tracer correlation factor obtained by the pair approximation coincides with the exact value of $1/3$, an almost exact agreement of the results is observed (Fig. 4). This shows that the pair approximation is quite acceptable for the calculation of $f^*(t)$. In a one dimensional case, a change in slope in the $\log f^*(t) - \log t$ curve is observed at the value of $f^*(t) \approx 0.1$ (Fig. 4) in agreement with the theory. With respect to the comparison with Monte-Carlo simulation, a small, but a systematic deviation of the simulation curve from that of the analytical value is observed in the range where t is large. Monte-Carlo simulation indicates a

slightly smaller value of $f^*(t)$ for the same value of t , although all the qualitative behavior is the same. At this moment, the origin of such a systematic deviation is unknown to us.

It is to be mentioned here that universal response is a property of the total assembly of charged particles and not that of the motion of a single particle in the assembly. In the case of the assembly of particles of the same species with a negligible amount of vacancies as treated here, the correlation effect for the assembly vanishes in the completely homogeneous case due to the indistinguishability among particles. In order to regain the correlation effect for the assembly of particles, it is necessary to deal with more general cases with mutual interactions among particles and a fluctuation in the distribution is necessary.

6. Universal Dynamic Response

So far, we have derived analytically that the relaxation motion of a single particle in a lattice gas is intrinsically non Debye and follows a typical KWW relaxation behavior even without any mutual interactions among mobile particles. Based on these analytical expressions, we would like to extract some rules with respect to the universal dynamic response.

In the previous section, for the assembly of particles of the same species with a negligible amount of vacancies, we saw that, although the KWW behavior is inherent, the effect is practically negligible except for the one dimensional case. The major cause for this is that $f^*(t)$ does not decrease enough for those cases. Solid electrolytes which follow the universal dynamic response commonly have very small values of tracer correlation factor. This indicates that more general models with interactions among mobile particles have to be introduced where $f(t)$ can decrease sufficiently. In our earlier publication [20], we discussed such general models and concluded that two kinds of generalized lattice gas models are sufficient to cover general cases; one with a large number of vacant sites with repulsive interactions among mobile particles, and the other, a mixture of two kinds of mobile ions with interactions which tends to create ordered distribution between the two kinds of particles. Using the latter model, we are able to discuss the origin of mixed alkali effect [21]. In this treatment, due to the necessity of introducing fluctuations (Eq. (11)), the

number of relaxation modes increases. In the pair approximation, the former requires two independent relaxation modes while the latter requires four independent relaxation modes.

The Jonscher's power exponent, p , is obtained as

$$\begin{aligned} -p &= d(\log f^*(t))/d(\log t) \\ &= \frac{f^{*'}(t)t}{f^*(t)} \end{aligned} \quad (17)$$

Here, the prime indicates the derivative with respect to t , and the time range where t is relatively large and $f^*(t)$ is close to the correlation factor f plays an important role. Equation (17) indicates the presence of the scaling factor $f^{*'}(t) \approx -\tau'$. In other words, the scaling factor is related to the rate of approach of τ to its limiting value.

As discussed in the previous section, there are two ways for τ in approaching its limiting value. When the correlation factor is not too small (the limiting value of τ is not too close to 1), τ approaches its limiting value exponentially, whereas when τ is close to 1 τ approaches $\tau(\infty)$ extremely slowly. In the range where τ approaches $\tau(\infty)$ exponentially, τ' is almost constant and p is inversely proportional to f according to Eq. (17) (Fig. 5).

Even in the case of multiple relaxation modes, the situation is not too different. Here, the $f^*(t) - t$ relation is a superposition of these modes and the mode with the smallest partial f plays the decisive role in determining p . This is because in the mode which has the smallest partial f , the time scale is the largest, and, hence, this mode determines the value of p . This serves as another scaling factor. In general, when the difference in the time scale between different modes is large, p is usually determined by the behavior in the mode with the smallest partial correlation factor. If the value of f is not close to zero in this mode, p is found to be inversely proportional to f^* (Fig. 5), while if f becomes extremely small, the scaling law appears and the value of p becomes relatively small.

However, no specific relation is found to exist in the scaling factor to make the value of p within one. Indeed, cases with p values larger than 1 are found [24].

7. Conclusion

Relaxation of a current when a constant field is switched on at $t=0$, in particular that of a single particle in the assembly, has been calculated analytically in a lattice gas model from the adiabatic state to the isothermal state with the same degree of rigor. The pair approximation of the PPM is utilized for the description of the adiabatic state, and its change with time is followed by the Bethe method in the form of the propagation of order. Our results show clearly that the relaxation motion of a single particle in a lattice gas is intrinsically non Debye and follows the KWW relaxation behavior even without any interaction among mobile particles. From this treatment, we can conclude the following:

- 1) The calculation can be extended easily to more general cases with interactions among mobile particles.
- 2) From such analytical expressions, the origin of the KWW behavior, and, hence, the universal dynamic response of assembly of particles can be extracted.
- 3) The origin of the KWW behavior is explained as being due to the return of the escaped vacancy with time while the jumping back process of the tagged particle into the vacancy it has left behind is being considered. More generally, the KWW behavior is due to a memory effect arising from the fact that it takes time for information to propagate over a distance by hopping.
- 4) The same relaxation process can be followed by a Monte Carlo simulation and the results support the above statements.

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References

1. A. K. Jonscher, *Nature* 267 (1977) 673.
2. K. Funke, "Jump Relaxation in Solid Electrolytes," in *Prog. Solid St. Chem.* vol. 22, pp. 1-95 (1993).
3. G. E. Murch and J. C. Dyre, *CRC Crit. Rev.* 15 (1989) 348.
4. C. Zener, *Elasticity and Anelasticity of Metals*, University of Chicago Press (1948).
5. J. C. Dyre, *J. Appl. Phys.* 64 (1988) 2456.
6. J. P. Bouchard and A. Georges, *Phys. Rep.* 195 (1990) 127.
7. K. L. Ngai, A. K. Rajagopal and S. Teitler, *J. Chem. Phys.* 88 (1988) 5086.
8. S. R. Elliott and A. P. Owens, *Phys. Rev.* B44 (1991) 47.
9. T. Ishikawa, K. Wada, H. Sato and R. Kikuchi, *Phys. Rev.* A33 (1986) 4164.
10. K. Wada, T. Ishikawa, H. Sato and R. Kikuchi, *Phys. Rev.* A33 (1986) 4170.
11. H. A. Bethe, *Proc. Roy. Soc.* 150 (1935) 552.
12. F. Zernike, *Physica* 1 (1940) 565.
13. H. Sato and R. Kikuchi, *Phys. Rev.* B28 (1983) 648.
14. K. Gschwend, H. Sato and R. Kikuchi, *J. Chem. Phys.* 69 (1978) 5006.
15. Y. Ozeki and T. Ishikawa, *J. Phys. Soc. Japan* 55 (1986) 3931.
16. H. Sato and H. Zhang, "Atomistic Approach to Diffusion in Ordered Alloys, edited by B. Fultz, R. W. Cahn and D. Gupta, *The Minerals, Metals and Materials Society* (1993) pp. 21-32.
17. H. Sato, *Nontraditional Methods in Diffusion*, edited by G. E. Murch, H. K. Birnbaum and J. R. Cost, *The Metallurgical Society of AIME* (1984) pp. 203-235.
18. H. Sato, S. A. Akbar and G. E. Murch, *Diffusion in Solids: Recent Developments*, edited by M. A. Dayananda and G. E. Murch, *Conference Proceedings, The Metallurgical Society of AIME* (1985) pp. 67-95.
19. H. Sato and A. Datta, *Solid State Ionics* 72 (1994) 19.
20. H. Sato, T. Ishikawa and K. Funke, *Solid State Ionics*, 53-56 (1992) 907.
21. H. Sato, "Theoretical Aspects of Mixed Alkali Effect," *Ceramic Transactions* vol. 20, *Glasses for Electronic Applications*, ed. K. M. Nair, *The American Ceramic Society* (1991) pp. 19-39.

22. R. Kikuchi and H. Sato, J. Chem. Phys. 55 (1971) 677.
23. R. Kikuchi and H. Sato, J. Chem. Phys. 57 (1972) 4962.
24. K. Funke, T. Mane, D. Wilmer, C. Cramer and T. Saatkamp, "Different Kinds of Localized Hopping in solid Electrolytes," in Ionic and Mixed Conducting Ceramics ed. by T. A. Ramanerayanon, W. L. Worrell and H. L. Tuller, The Electrochemical Society, Inc. (1994) p. 564-573.

Figure Captions

- Fig. 1. Normalized relaxation curve. The quantity $f^*(t)$ represents the time dependent correlation factor.
- Fig. 2. The jump back process of the tagged particle (represented by an asterisk) in a disordered binary alloys by means of the pair approximation of the PPM.
- Fig. 3. $\tau - t$ relations for structures with different coordination numbers, $2\tilde{\omega}$.
- Fig. 4. Comparison of Monte Carlo simulation results with the analytical theory for $2\tilde{\omega} = 2$ and for $2\tilde{\omega} = 3$.
- Fig. 5. The relation between p and f^* .
 - a) Single mode. p and f^* for $2\tilde{\omega} = 2, 3, 4$ and 6
 - b) Two mode case. p and f for a large concentration of vacant sites.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

(a)

(b)

Fig. 5