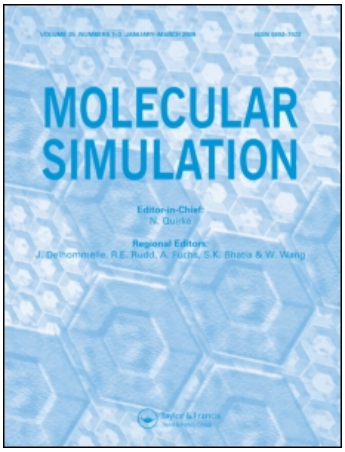

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MECHANISM OF THE ATOMIC INTERMIXING PROCESS IN CRYSTALLINE MICROCLUSTERS

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The Mechanism of atomic intermixing process in crystalline microclusters is studied by molecular dynamics simulation for a two-dimensional system with the Lennard-Jones potential. Temperature is chosen so that a cluster consists of solid-like core region and the region of surface melting. It is found that atomic intermixing in the solid-like core region is caused by the motion of a dislocation through the cluster as well as the random walk of a vacancy in the cluster. Generation of a dislocation or a vacancy occurs at the interfacial region between the liquid-like surface and the solid-like core regions due to large scale fluctuation of the configuration of atoms in the region of surface melting and the opportune collective motion of atoms in the solid-like core region. The rate per atom of atomic intermixing, the basic quantity of our interest (for the definition see the text), in the solid-like core of the microcluster is three to four orders of magnitude larger than that in the bulk crystal.

KEY WORDS: Microcluster, atomic intermixing, molecular dynamics simulation.

1 INTRODUCTION

One of the interesting properties of crystalline microclusters is their pronounced intermixing. Coalescence growth of Fe and Ni clusters occurs above 473 K in a short time (10^{-2} to 10^{-3} seconds) to form the ordered phase as reported by Kaito and coworkers [1,2]. Homogeneous alloying of crystalline Cu and Au clusters deposited on an amorphous carbon film proceeds in less than 30 seconds at room temperature as reported by Mori and coworkers [3, 4, 5]. If we estimate the diffusion coefficients required for these processes, they must be many orders of magnitude larger than those for the bulk.

To understand the reason behind the phenomena and gain insight into atomic intermixing mechanisms characteristic of microclusters, we have employed molecular dynamics simulation. We employ two-dimensional system of atoms interacting with the Lennard-Jones potential in the present paper rather than three-dimensional systems with potentials which are more realistic for the experimentally investigated systems. We regard the observation of the animated motion of atoms as crucially

important in gaining insight to the problem, and the employment of two-dimensional systems is essential to achieve this purpose. Since qualitative understanding toward the nature of the problem is aimed as the first step, the Lennard-Jones potential is considered to be sufficient. Further, we study the atomic intermixing mechanism in a single component cluster instead of interdiffusion in binary systems in the present paper.

In our first paper [6], we carried out the molecular dynamics simulation also for the two-dimensional single component Lennard-Jones system and found that the diffusion coefficients in the crystalline microclusters, which contain the regions of surface melting, are not much smaller than that in the bulk liquid. In the simulation we had chosen initial velocities of atoms so that the clusters satisfy the condition that the total linear and angular momenta vanish. However, the values of linear and angular momenta for the solid-like core region alone of each cluster might not have been negligible. Hence, the mean square displacements evaluated for the solid-like core regions might have contained an irrelevant contribution due to translational and rotational motions of that region as a whole. In fact, in our second paper [7], it was found by the detailed observation of the rearrangement process of atoms that only about a half of the mean square displacement evaluated in the first paper should have been attributed to the atomic intermixing process.

In the present paper, we employ the local coordinate frame for the solid-like core region to eliminate the contribution to the mean square displacement from the translational and rotational motions of that region as a whole. To clarify the mechanism of atomic intermixing, we pursue the detailed direct observation of the rearrangement process of atoms as done in the second paper [7]. Finally, diffusion of a vacancy in the bulk crystal is studied to make the numerical comparison between the atomic intermixing rates in the bulk and in the solid-like core region of a microcluster.

2 PROCEDURE OF SIMULATION

We use the molecular dynamics method for simulation of a single component system with the Lennard-Jones potential

$$\phi(r_{ij}) = 4\varepsilon\left\{\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right\}, \tag{1}$$

where r_{ij} is the distance between the atoms i and j. We employ the Verlet algorithm for integration with a time step of 0.0259τ, where τ represents

$$\tau = \sqrt{\frac{m\sigma^2}{4\varepsilon}}, \tag{2}$$

in which m denotes the mass of an atom. The cut-off radius of the potential R_c is 3.5σ.

We prepare a two-dimensional model with the triangular lattice for a microcluster. The model is prepared by arranging atoms in a hexagonal shape with the lattice constant of the bulk crystal at 0 K and by assigning them velocities under the condition that the total linear and angular momenta vanish. The total number of atoms in a cluster is chosen to be 331. The actual size of the cluster for which the data are taken may become slightly smaller due to evaporation of atoms. We place the cluster in a square with the periodic boundary and raise the temperature to the desired value by linearly increasing the velocities of atoms. The temperature adopted is 0.375 in the unit of ε/k_B, where k_B denotes Boltzmann's constant. This temperature is lower than that of the triple point [8] for the two-dimensional Lennard-Jones system. After the temperature reached the desired value, it is adjusted at every time step for the first 1000 steps (25.9τ) for aging. Then, the system is isolated afterwards for 240000 steps (6216τ). The numerical data were saved at every 100 steps. As seen in Figure 1 the system is in equilibrium after the aging process, and the fluctuation from one "phase" to the other "phase" as found by Jellinek *et al.* [9] is not observed in 6216τ in the present simulation.

Figure 2 shows the trajectories of atoms on the coordinate frame with respect to which the total linear and angular momenta vanish for the atoms within the classifying circle which is to be defined. We see that at $T=0.375\varepsilon/k_B$ the cluster consists of solid-like core region and the region of surface melting, although the boundary is not well-defined. Here, an atom is regarded as solid-like when its trajectory over 350τ or more may be considered as indicating vibration around a lattice site. Since the aim of the present work is to get insight into the mechanism of atomic intermixing in microclusters having a crystalline lattice structure, we focus our attention only on the solid-like core region when we evaluate for example the mean square displacement of atoms. To facilitate the computational procedure we employ a classifying circle so that atoms within it may be considered as solid-like. The center of the circle is chosen to coincide with the center of mass of the cluster and its radius is chosen somewhat arbitrarily to be 6.0σ. This value is determined by a trial and error method. The trajectories of atoms within a chosen classifying circle and their power spectrum, *i.e.* the Fourier transform of the velocity autocorrelation function, are

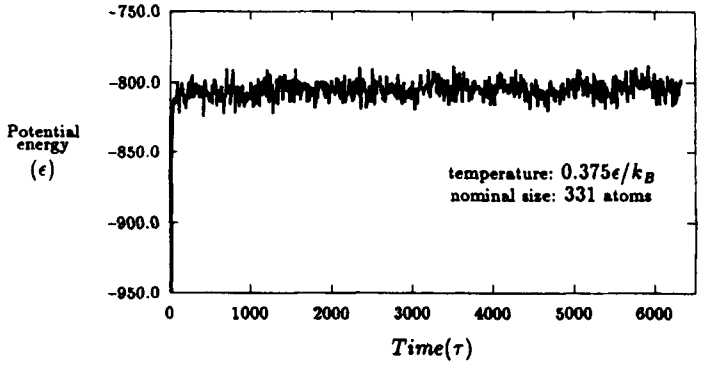

Figure 1 Change of the potential energy with time for the cluster over 6212 τ.

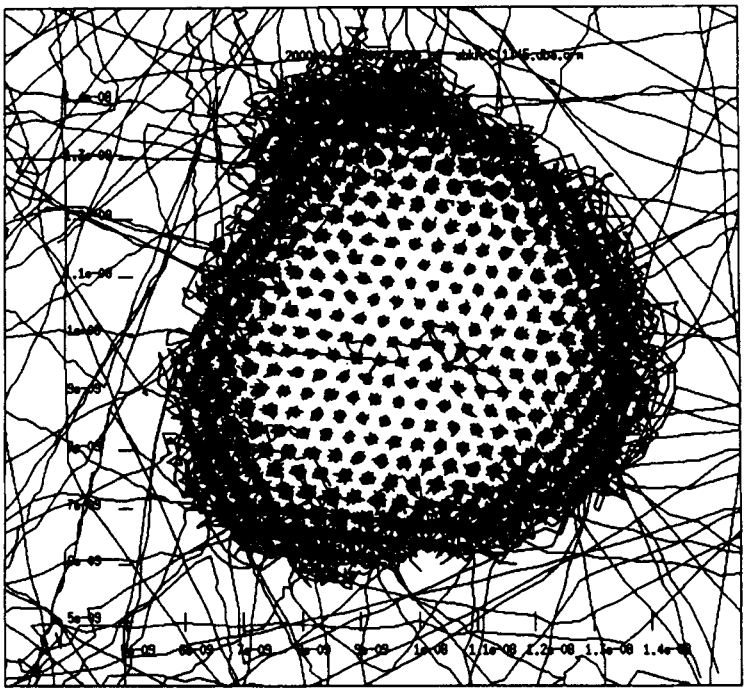

Figure 2 Trajectories of atoms in the cluster for the period from 200000 to 235000 steps ($5180\tau \sim 6086.5\tau$) on the local coordinate frame with respect to which the total linear and angular momenta vanish for the atoms within the classifying circle.

employed for judgement [9]. We then introduce a local coordinate frame with the origin at the center of mass of atoms within the classifying circle in such a way that the total linear and angular momenta of those atoms relative to the frame vanish [10]. Data obtained by simulation are transformed into those with respect to the local frame and they are used for the analyses. Wavy trajectories for evaporated atoms in Figure 2 are caused by the data transformation described above. When some atoms cross the circle, we use new set of atoms within the circle to redefine the local frame.

3 RESULTS AND DISCUSSION

3.1 Atomic Intermixing in a cluster

Plot of the mean square displacement vs time is shown in Figure 3 for the atoms inside the classifying circle. Note that no linear increase is observed and that there exist jumps with the plateaus between them except at the last part which is more complex. Hence, the usual procedure of evaluating the diffusion coefficient from the slope cannot be employed in the present case. The power spectrum calculated from

the data corresponding to one of the plateaus in Figure 3 is shown in Figure 4. Note the zero value at the zero frequency, which means that rigid body like translation and rotation of the atoms within the classifying circle are eliminated by employing the local frame. It is expected that jumps in Figure 3 reflect the occurrence of large scale atomic intermixing, and for each jump we make detailed studies of the trajectories to find out the mechanism causing it. On the other hand, plateaus are supposed to indicate vibrations of atoms around lattice sites, and this supposition is confirmed by the observation of the trajectories and the power spectrum.

Figure 5 shows the trajectories over the period between 15000 and 21000 steps ($388.5\tau \sim 543.9\tau$) which contains the first jump in Figure 3. We see collective displacements of atoms. To find out the detailed process causing these collective displacements, snap shots are taken as shown in Figures 6a to 6d. We observe that the collective displacements result from the motion of a dislocation. After the dislocation passes through the cluster, the lattice order recovers but the resultant change of sites for atoms is induced.

The trajectories corresponding to the continuously increasing last part in Figure 3 are shown in Figure 2. We see the diffusion-like displacements of atoms passing through lattice sites. To find out the details of this process, snap shots are taken as shown in Figures 7a to 7d. In Figure 7a we observe fluctuation in the atomic arrangement in the lower left hand region outside the classifying circle and the opportune collective displacements inside the circle. As a result a vacancy is generated as shown in Figure 7b and it moves randomly as seen in Figures 7c and 7d.

Since atomic intermixing is meaningful only when atoms are mutually distinguishable, it refers to the interchange of sites between distinct isotopic atoms in the case of single component systems. The rate per atom of atomic intermixing, the basic quantity of our interest, is defined as the frequency with which a given atom surrounded by the other isotopes changes its site. This frequency corresponds to that with which a given atom is in the activated state during the process of changing its site. In the molecular dynamics simulation we number identical atoms, which may be interpreted as a system of distinct isotopes with the negligible mass difference. Hence, the rate per atom of atomic intermixing may be evaluated as the value

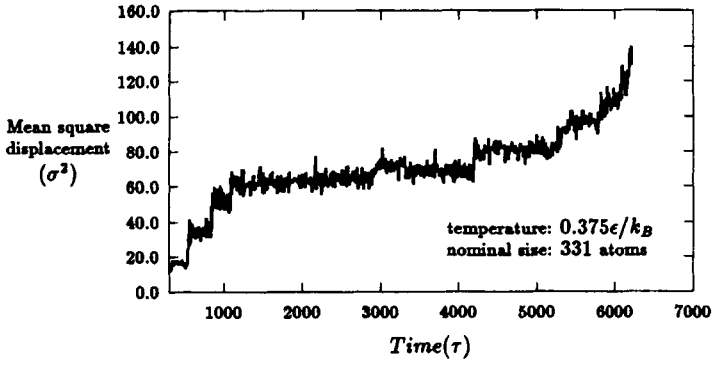

Figure 3 Mean square displacement of atoms within the classifying circle with respect to the local frame.

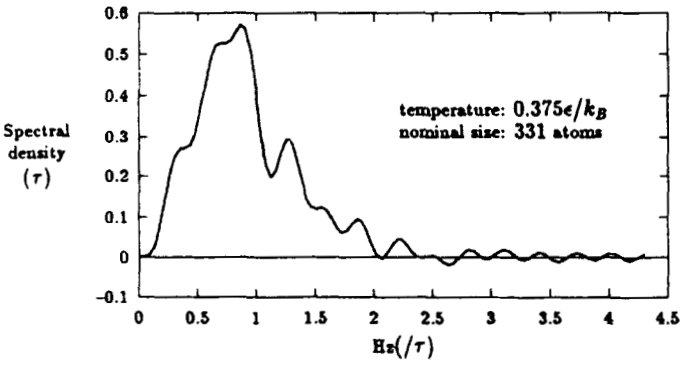

Figure 4 Power spectrum corresponding to a plateau in Figure 3 for the atoms within the classifying circle with respect to the local frame.

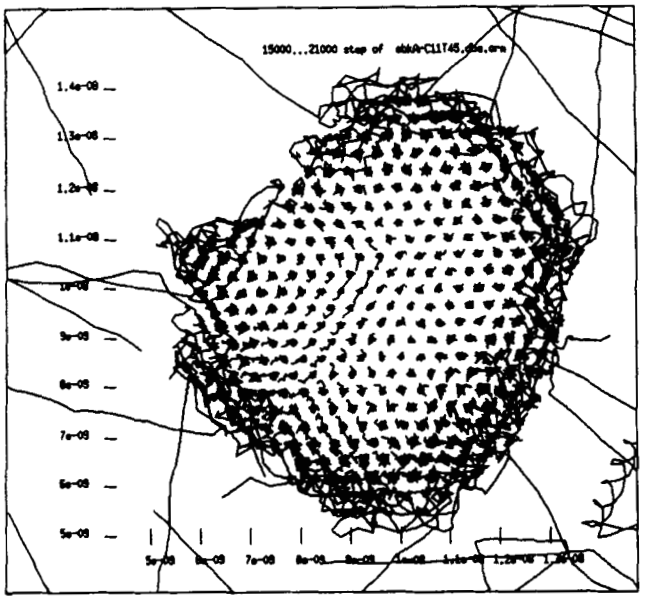

Figure 5 Trajectories of atoms in the cluster for the period from 15000 to 21000 steps ($388.5\tau \sim 543.9\tau$) on the local frame.

obtained by counting the frequency with which atomic configuration somewhere in the region of interest is brought to the activated state and then dividing the result by the number of atoms in that region.

Thus, the rate per atom of atomic intermixing within the classifying circle is given by

$$R_{\mathrm{cl}} = \frac{N}{T_{\mathrm{obs}} N_p}, \tag{3}$$

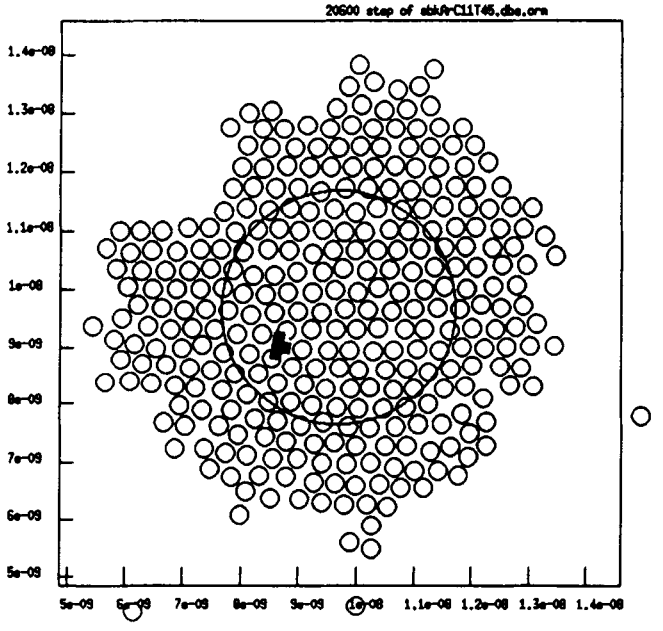

Figure 6a Snap shot of the cluster with a dislocation at 20600 step (533.5τ).

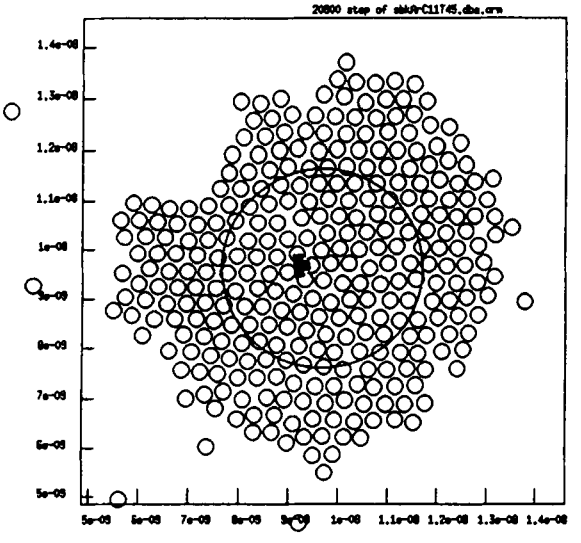

Figure 6b Snap shot of the cluster with a dislocation at 20800 step (538.7τ).

where N denotes the total number of occurrence of activated-state configurations corresponding to the change in sites during the whole period of the simulation T_{obs} and N_p the number of atoms in the classifying circle.

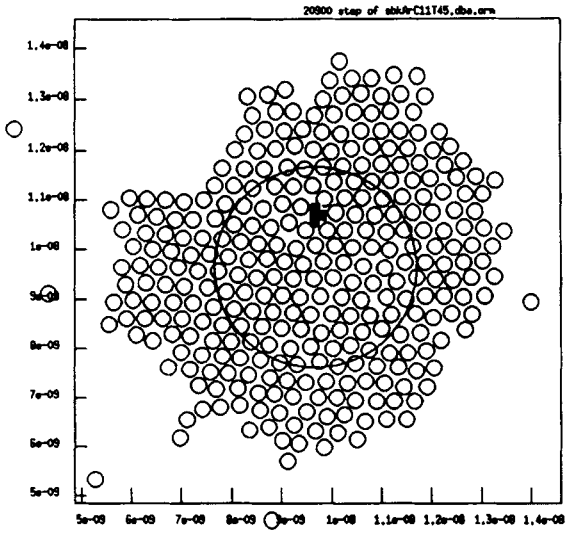

Figure 6c Snap shot of the cluster with a dislocation at 20900 step (541.3τ).

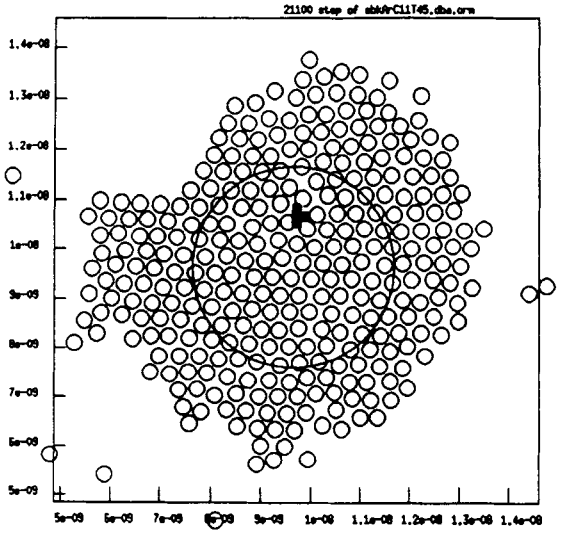

Figure 6d Snap shot of the cluster with a dislocation at 21100 step (546.5τ).

The data in the present simulation are as follows. N is obtained as 57 by counting the occurrence from the snap shots and the trajectories, in which 26 and 31 are due to dislocation and vacancy mechanisms, respectively. T_{obs} is $240000 \times 0.0259\tau$ and N_p is about 96. So the atomic intermixing rate per atom in the solid-like region of a cluster is found to be $R_{cl} = 9.6 \times 10^{-5} / \tau$.

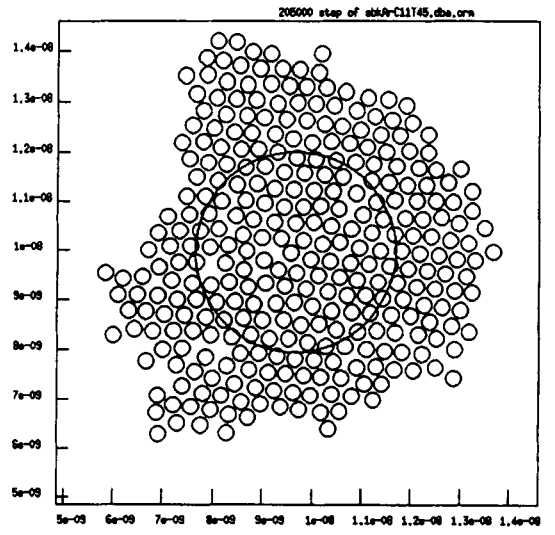

Figure 7a Snap shot of the cluster with a vacancy at 205000 step (5309.5τ).

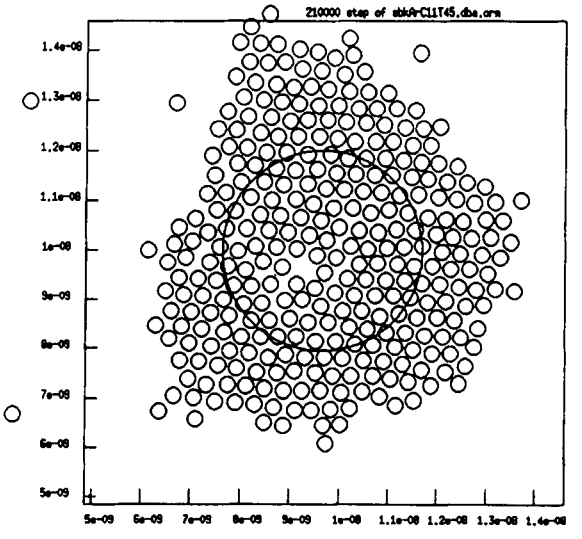

Figure 7b Snap shot of the cluster with a vacancy at 210000 step (5439τ).

3.2 Atomic Intermixing in the Bulk Crystal

To make the numerical comparison of the atomic intermixing rate per atom between the solid-like core region of a microcluster and the bulk crystal, we perform a molecular dynamics simulation study of the vacancy diffusion in the bulk crystal. Studies on the following two aspects are required: 1) Calculation of the vacancy

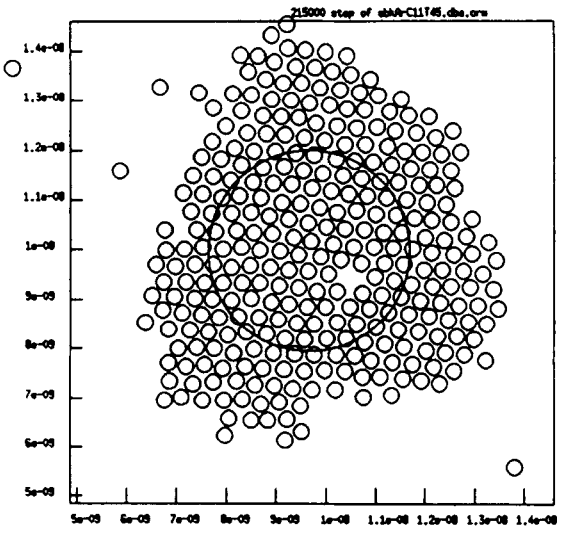

Figure 7c Snap shot of the cluster with a vacancy at 215000 step (5568.5τ).

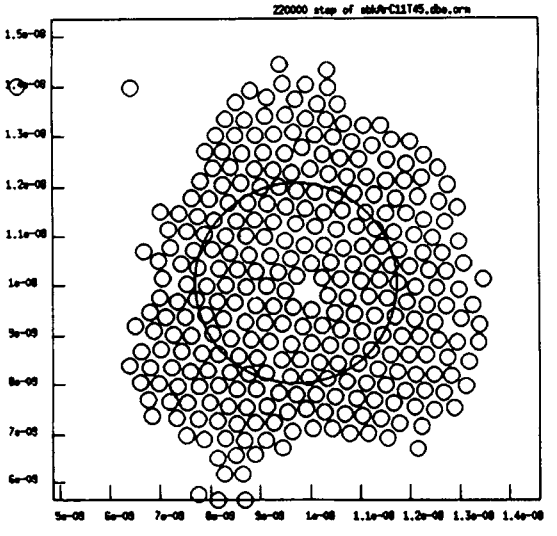

Figure 7d Snap shot of the cluster with a vacancy at 220000 step (5698τ).

formation energy in the bulk crystal, which is needed to evaluate the fraction of vacancies at thermodynamic equilibrium, and 2) frequency with which one vacancy jumps from site to site in the bulk crystal. The model for the bulk crystal is prepared by arranging 647(= 648 − 1) atoms in a rectangular region with the periodic boundary as shown in Figure 8. The system is divided into two parts, regions A(336 atoms)

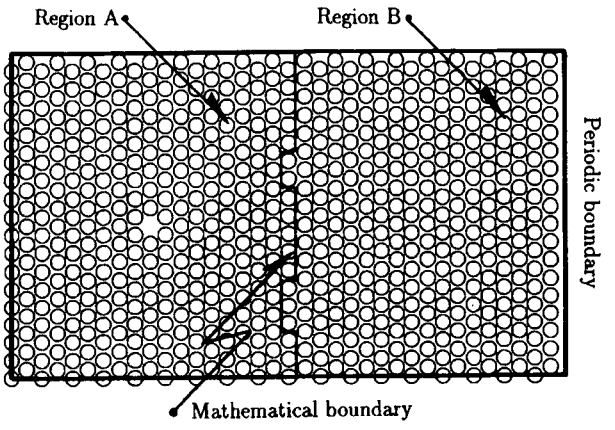

Figure 8 Initial configuration of atoms for the bulk crystal in which the lattice constant is 1.1588σ.

and B(331 atoms), by a mathematical boundary and one vacancy is introduced in the region A. Role of the mathematical boundary is just for the convenience of simulation and it does not cause any physical effect. Lattice constant 1.1588σ for the bulk crystal at $T=0.375\varepsilon/k_B$[11] is used and the system is made equilibrium at $T=0.375\varepsilon/k_B$. Pressure is evaluated to be $0.126\varepsilon/\sigma^2$ by the virial theorem. The numerical data were saved at every 10 steps after the aging process.

After the aging process at $T=0.375\varepsilon/k_B$, potential energies are evaluated for the atoms contained in the regions A and B, respectively. Interaction of atoms beyond the mathematical boundary is of course taken into account. The results are plotted against time in Figure 9. Distributions of the values are given in Figure 10 and the

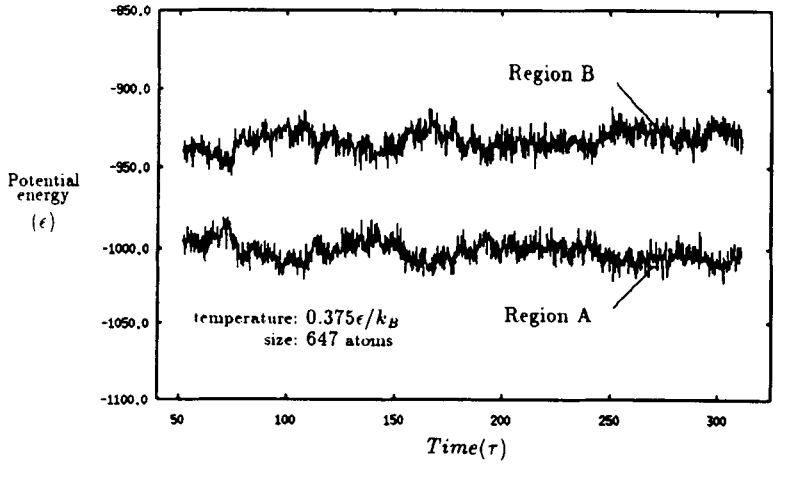

Figure 9 Time variations of potential energies the atoms contained in the regions A and B in Figure 8 at $T=0.375\varepsilon/k_B$.

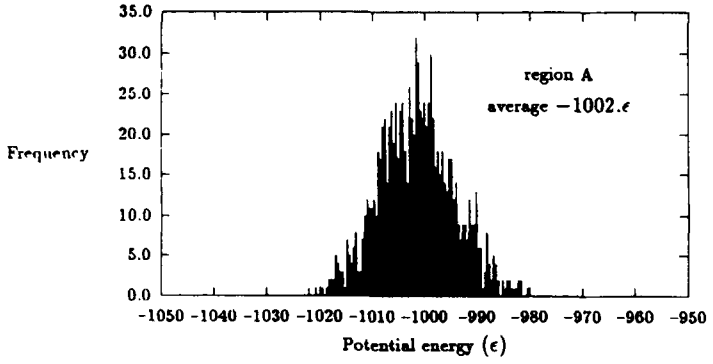

Figure 10a Distribution of the potential energy for the region A which is shown in Figure 9.

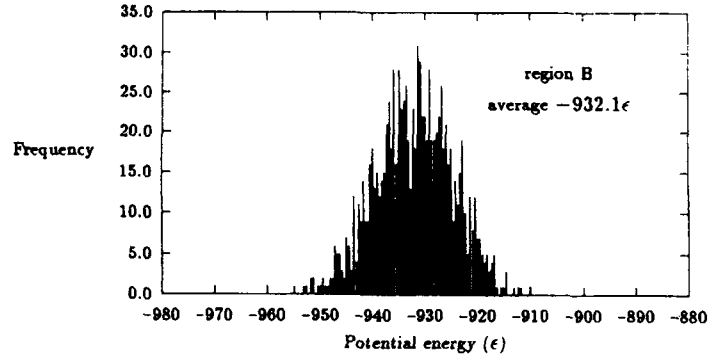

Figure 10b Distribution of the potential energy for the region B which is shown in Figure 9.

averages U_A and U_B are evaluated to be $-1.00151 \times 10^3\ \varepsilon$ for the region A and $-9.32065 \times 10^2\ \varepsilon$ for B with the standard deviation about 12ε. Potential energy Δu_v for forming a vacancy is given by

$$\Delta u_v = \left[U_A - (336+1)\frac{U_B}{311} \right] + \frac{U_B}{311}, \tag{4}$$

which results in $\Delta u_v = 5.5\varepsilon$. Note that the choice of the system as shown in Figure 8 ensures the equality of temperature in computing U_A and U_B. Fraction of the vacancy site in the bulk crystal is given by

$$P_v = e^{-\Delta u_v / k_B T}, \tag{5}$$

where we neglect the entropy of vacancy formation. The vacancy formation entropy results from the change in the vibrational entropy and it may be roughly estimated

as $(6/2)k_B \ln [\kappa_B/\kappa_v]$, where κ_B and κ_v denote spring constants for a bulk atom and an atom next to a vacancy, respectively. If we take $\kappa_B/\kappa_v = (6/5)$ as a rough estimate, $-(6/7)\, k_B T \ln [\kappa_B/\kappa_v]$ is estimated to be -0.2ε, which may be neglected in comparison with $\Delta u_v = 5.5\varepsilon$.

The rate per atom of atomic intermixing in the bulk crystal is given by

$$R_{bk} = \frac{N_v}{T_{\text{obs}}} P_v, \tag{6}$$

where N_v denotes the number of jumps of the vacancy during the simulation period T_{obs}. Figure 11 shows the trajectories of atoms for the region A and we see that $N_v = 14$ in $T_{\text{obs}} = 259\tau$. Employing $\Delta u_v = 5.5\varepsilon$, the atomic intermixing rate per atom is found to be $R_{\text{bk}} = 2.4 \times 10^{-8}/\tau$.

Thus, the rate per atom of atomic intermixing in the solid-like core of a cluster is found to be three to four orders of magnitude larger than that in the bulk crystal. However, we have not considered the possibility of atomic intermixing due to motion of dislocations in the bulk crystal. Although dislocation does not exist in a three-dimensional crystal at equilibrium, it may exist in a two-dimensional bulk crystal. Nevertheless, it is not considered worthwhile to pursue the very complex problem of dislocation mechanism of atomic intermixing in a two-dimensional bulk crystal, because our final purpose is to get insight into the mechanism of extremely fast atomic intermixing in three-dimensional crystalline microclusters. Since the contributions due to vacancy and dislocation mechanisms to the rate of atomic intermixing in a cluster are found to be similar magnitude, the conclusion stated above is basically unaltered even when we take only the vacancy mechanism into account.

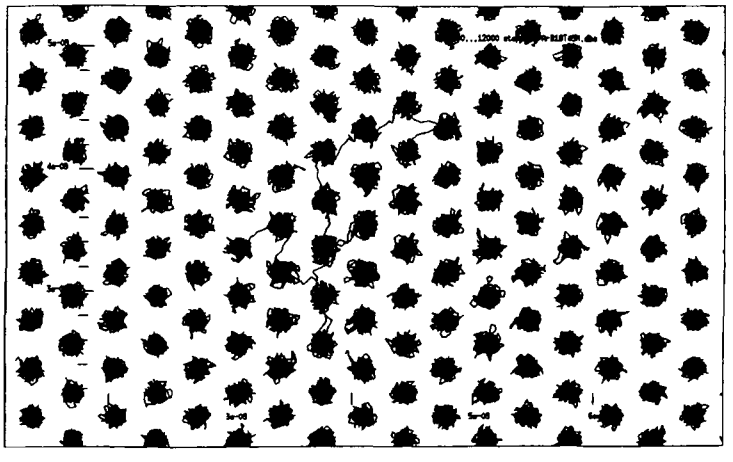

Figure 11 Trajectories of atoms for the region A over 259τ.

4 CONCLUSION

Molecular dynamics simulation is carried out to study the mechanism of atomic intermixing process in crystalline microclusters. Two-dimensional system with the Lennard-Jones potential is employed and the temperature is chosen so that a cluster consists of solid-like core region and the region of surface melting. We employ the local coordinate frame for the solid-like core region to eliminate the contribution of rigid body like translation and rotation of the region.

It is found that atomic intermixing in the solid-like core region is casued by the motion of a dislocation through the cluster as well as the random walk of a vacancy in the cluster.

Generation of a dislocation or a vacancy occurs at the interfacial region between the liquid-like surface and the solid-like core regions due to large scale fluctuation of the configuration of atoms in the region of surface melting and the opportune collective motion of atoms in the solid-like core region.

The rate per atom of atomic intermixing in the solid-like core of the microcluster is three to four orders of magnitude larger than that in the bulk crystal.

Acknowledgements

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References

[1] C. Kaito, Y. Saito and K. Fujita, "Ordered structure in alloy grains of iron-nickel produced by the gas evaporation technique", *Jpn. J. Appl. Phys.*, **28**, L694 (1989).
[2] C. Kaito and Y. Saito, "Ordered Grains produced by Coalescene of Fe and Ni Smoke Grains", *Proc. Japan Acad.*, **65**, Ser. B, 125 (1989).
[3] H. Mori, M. Komatsu, K. Takeda and H. Fujita, "Spontaneous alloying of copper into gold atom clusters", *Phil. Mag. Lett.*, **63**, 173 (1991).
[4] H. Yasuda, H. Mori, M. Komatsu, K. Takeda and H. Fujita, "In situ observation of spontaneous alloying in atom clusters", *J. Electron Microsc.*, **41**, 267 (1992).
[5] H. Yasuda, H. Mori, M. Komatsu and K. Takeda, "Alloying behavior of gold atoms into nm-sized copper clusters", *Appl. Phys. Lett.*, **18**, 2173 (1992).
[6] M. Okada, H. Yoshimoto and K. Nishioka, "Molecular dynamics simulation of self diffusion in microclusters", *Molecular Simulation*, **14**, 67 (1995).
[7] H. Yoshimoto, M.Okada and K. Nishioka, "Mechanism of self diffusion in microclusters", *Proc.* ISSPIC7, *Sep.*, 1994, Kobe, Japan, in print.
[8] F. F. Abraham, "Melting in two dimensions is first order: an isothermal-isobaric Monte Carlo study", in Ordering in Two Dimensions, ed. S. K. Sinha, (Elsevier North Holland, Inc., New York, 1980), pp.155–161.
[9] J. Jellinek, T. L. Beck and S. Berry, "Solid-liquid phase changes in simulated isoenergetic Ar13", *J. Chem. Phys.*, **84**, 2783 (1986).
[10] K. Nishioka, G. M. Pound and F. F. Abraham, "Coordinate Transformation for Separating the Classical Phase Integral and the Rotational Partition Function of a Small Liquid Cluster of Molecules", *Phys. Rev. A*, **1**, 1542 (1970).
[11] K. Tokuda, Dissertation [in Japanese], Department of Mechanical Engineering, University of Tokushima (1991).