Particle Diffusion in Correlated Disordered Media near Transition Point

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Particle diffusion of ions is investigated in a super-ionic conductor AgI in the liquid and α states near the melting point by observing the non-Gaussian parameter, the mean square displacement, the distribution function of particle and the intermediate function of density auto-correlation. Anomalous properties of particle diffusion are confirmed in the super-ionic conductor AgI, on some intermediate time range of the order of 1ps-30ps.

§1. Introduction

It is well-known that anomalous dynamical properties such as subdiffusive behavior of the mean square displacement (MSD) and as α and β type decay of the density auto-correlation function exist on some intermediate time scale in super-cooled liquids near the glass transition.[1)] These anomalous properties exhibit non-Gaussian processes.

It has also been reported by the authors by means of molecular dynamical (MD) simulation that the time development of the distribution function $P(x,t)$ of the particle displacement does not obey normal Gaussian process on a similar time scale in the liquid state near the melting temperature T_m and in the α-phase of AgI in thermal equilibrium.[2)]

In this paper we try to reinvestigate the super-ionic conductor AgI numerically by the MD method in the light of the recent study of the slow dynamics mentioned above. We observe, in addition to the MSD and the non-Gaussian parameter (NGP), the self part of the density auto-correlation function $F_s(k,t)$, which is the Fourier transformation of the distribution function $P(x,t)$ of the diffusing particles in the position x.

In the function $F_s(k,t)$, which is also directly related to the dynamical structure factor $S(k,\omega)$ by Fourier transformation of the time variable t, the α and β relaxation processes have been observed.[1)] In addition, the numerically obtained distribution function $P(x,t)$ also has complementary information about the anomalous dynamical properties. It is thus worth revisiting this anomalous diffusion process in AgI by examining both the function $F_s(k,t)$ and the distribution function $P(x,t)$.

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§2. Numerical calculation

A system of 108 AgI particles in a fixed cubic box with periodic boundary conditions is described by the following effective pair-potential for each i, j pair

$$V_{ij}(r) = H_{ij}/r^{n_{ij}} + Z_i Z_j/r - P_{ij}/r^4 - W_{ij}/r^6, \qquad (2\cdot1)$$

which has been initially used by Parrinello et al.[3] Values of the parameters in the potential are the same as those used in Ref. 2). When the temperature T is between the super-ionic transition point $T_c = 480$ K and the melting temperature $T_m = 910$ K, the system is in the super-ionic phase or α-phase in thermal equilibrium in which Ag ions diffuse. We achieve four states at 1GP, (1) the liquid state at 1500 K, (2) the liquid state at 940 K near T_m, (3) the α-state at 850 K near T_m, and (4) the α-state at 530 K. For each case, the initial condition refers the liquid state at 1500 K. One computer step corresponds to 2.785×10^{-3} ps. The numerical data are picked out from the MD calculation of the last 40×10^4 steps, discarding the initial 30×10^4 step. The results are the followings.

§3. Results and discussion

The NGP of Ag and I ions at various temperatures are shown in Fig. 1 as a function of time t in ps.

I ions of Case (2) (940 K) take a fairly large value of NGP on the time range up to 30 ps, while the other cases seem to be normal. NGP of Ag ions in Cases (2) (940 K), (3) (850 K) and (4) (530 K) also tend to deviate from the normal value of zero. The corresponding MSD are shown in Fig. 2. A cross-over from ballistic diffusion ($\propto t^2$) to normal diffusion of liquid (or liquid-like) state or to localization (solid-like state) is observed on the time range of 0.1 ps-1 ps. Especially in Case (2) of I ions and Cases (2), (3) and (4) of Ag ions, a hump is observed on the time

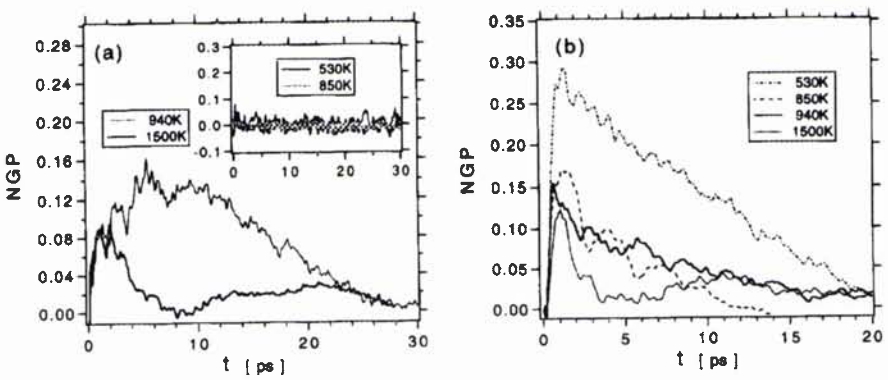

Fig. 1. Time dependence of NGP of (a) I ions and (b) Ag ions at various temperatures.

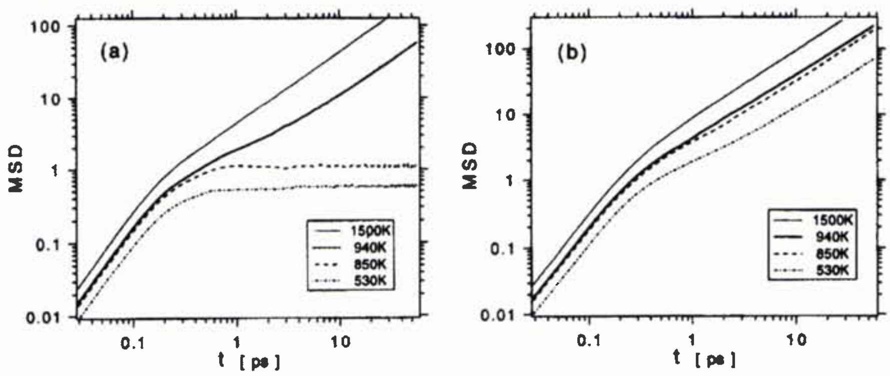

Fig. 2. Log-log plot of the time dependence of MSD of (a) I and (b) Ag ions at various temperatures.

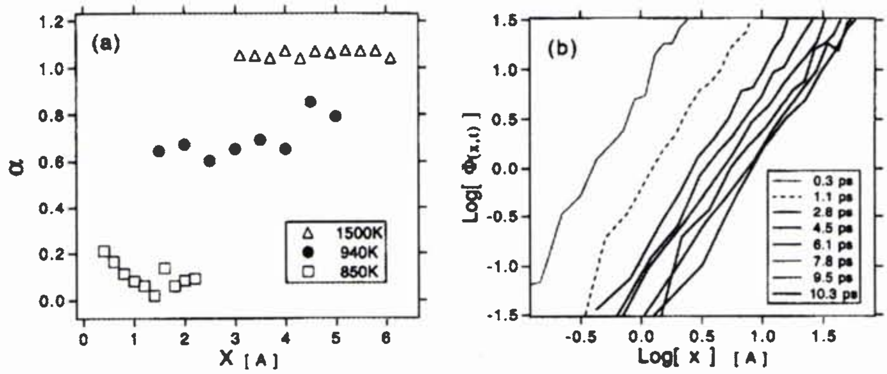

Fig. 3. (a) Estimated value of the index of power α of t in the entropy function $\Phi(x,t)$ of I as a function of x at various temperatures. (b) Log-log plot of the entropy function of I as a function of the displacement x for various values of time t on the time range of 0.1 ps-10 ps in the case of $T = 940$ K. On this time range, the value of β is less than but close to 2.

region around 1 ps. This hump of MSD suggests a sub-diffusion process due to the trapping mechanism, or due to the shrinked dimension of the diffusing path.

The distribution function $P(x,t)$ of I ions is analyzed in Fig. 3 as an example. The entropy function $\Phi(x,t) = -\log[P(x,t)/P(0,t)]$ has been assumed to have the form,[2)]

$$\Phi(x,t) = \Omega(x)/t^{\alpha}, \quad \Omega(x) = x^{\beta}. \tag{3·1}$$

The indices of the power α and β describe Gaussian process when $\alpha = 1$ and $\beta = 2$. Deviation from Gaussian process is observed in the values of α and β in Case (2) on the time range near and after the hump of MSD, and also in Cases (3) and (4) on the intermediate time region. Similar trend is observed also for Ag ions corresponding

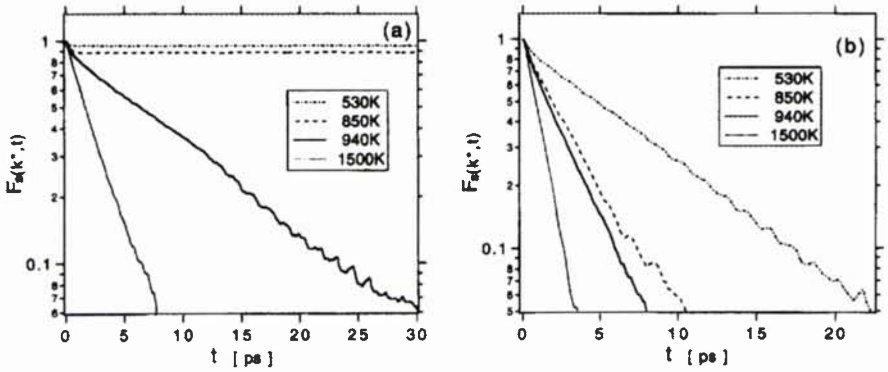

Fig. 4. Intermediate function $F_s(k^*,t)$ of (a) I and (b) Ag ions as a function of time for a specific wave number k^*.

to the abnormalities of the NGP and MSD. The results are consistent with those in Ref. 2).

The intermediate function $F_s(k,t)$ is shown in Fig. 4 for I and Ag ions for a wave vector $k^* = 2\pi \frac{2}{3\sqrt{3}l} \times (1,1,1)$ where l is the lattice constant of α-state. In the states (3) and (4) of α-phase, the intermediate function $F_s(k^*,t)$ of I ions exhibits solid-like feature, while in the liquid states (1) and (2), it exhibits normal Debye relaxation process (proportional to $\exp(-t/\tau)$). No remarkable deviation from the Debye relaxation is found in the Fig. 4 even though some of the corresponding distributions $P(x,t)$ of particle displacement have anomalous feature.

To summarize, particle diffusion in the super-ionic conductor AgI has been numerically investigated by observing the NGP, MSD, distribution function of diffusing particles and the intermediate function of the density auto-correlation function. Most of the results are consistent with those in the previous study [2] and some anomalous diffusions are confirmed in the distribution function $P(x,t)$ of the particle displacement. However, the corresponding intermediate function does not seem to show anomalous behavior. Details for longer time simulation is now being studied and the results will be published elsewhere. [4]

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