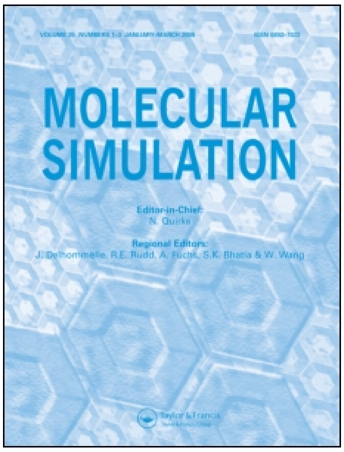

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Ionic Dynamics of Alkali Chloride Systems in the Supercooled and Glassy States: Analyses of Inherent Structures

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IONIC DYNAMICS OF ALKALI CHLORIDE SYSTEMS IN THE SUPERCOOLED AND GLASSY STATES: ANALYSES OF INHERENT STRUCTURES

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Molecular dynamics simulations have been performed for two alkali chlorides, LiCl and LiCl-KCl, to investigate the relation between the finite-temperature real properties and the corresponding configurations of potential minima (Stillinger's inherent structures). The thermodynamic properties and the single-particle dynamical properties relevant to not vibrational but diffusive motions have been analyzed on the basis of quenched inherent structures. Each system include so large enthalpy gap and so large enthalpy fluctuation in their quenched configurations at around the glass transition temperature that both systems are found to be fragile liquids in Angell's scheme. It is found that the mean square displacements in the successive inherent structures exhibit Brownian behavior or linear time-dependence from very early time $t = 0.01$ ps, so that interbasin transitions represent the ionic diffusive behavior. The interbasin transitions can successfully describe Chemla's effect and an inverse phenomenon observed in real MD trajectory of the low-temperature liquids and glasses. Furthermore, we have revealed that there are three types of short-time intermittent interbasin transitions, namely, the jump-type transitions, non-jump-type residual motions, and residence in basins, all of which are hidden under vibrational motions at finite temperatures. As for the chemical difference, there are more prominent residual motions which are distinguished from the jump-type transitions in the LiCl-KCl glass than in the LiCl glass.

KEY WORDS: Molecular dynamics, inherent structure, alkali chlorides, fragile liquid, interbasin transition, Chemla's effect.

1 INTRODUCTION

For many years it has been unclear how chemical differences between materials would influence their glass-forming ability and even how they would affect the diffusive dynamics in the low-temperature liquids. In this connection, Angell has proposed the concept of *strong* and *fragile* liquids on the basis of measured viscosity and heat capacity of various glass-forming liquids [1]. Thermodynamically the former has small or no heat capacity change at the glass transition, while the latter has a large change. It has been believed that the observed general characteristics in thermodynamic and transport properties of strong and fragile liquids can possibly be understood by considering the relation between the topographical characteristics of potential surfaces and the finite-temperature motions excited on them [1].

In this idea, Stillinger and Weber's concept of inherent structures is a useful tool to elucidate the particle dynamics on the configurational-space potential surfaces of the physical systems [2]. Inherent structures are spatial configurations of particles in local potential minima hidden under real molecular dynamics trajectory. Indeed, the concept of inherent structures has been utilized in molecular dynamics studies to investigate the thermodynamic properties and short-time dynamics of various condensed matter [3]. The thermodynamic functions of liquids can be evaluated in terms of normal modes in inherent structures or quenched configurations [4]. In fact, for collective dynamics, one of us successfully represented the dynamical structure factors $S(k, \omega)$ of alkali chloride glasses in terms of the normal modes [5]. This shows that the collective vibrations of ions in glassy state are constructed in terms of intrabasin vibrations in the inherent structures. In this analysis, however, it was found that there were not normal modes less than $\omega < 2$–$3\ \mathrm{cm}^{-1}$[6]. It is therefore impossible to represent any lower frequency modes or ionic diffusive motions ($\omega = 0\ \mathrm{cm}^{-1}$) in terms of the normal modes (vibrations in potential basins). Certainly it has been reported that there is a correlation between the direction of spatial transition of particles and the lowest-frequency normal mode vector [7]. Nevertheless, our present policy is to examine whether self-diffusion of particles can be represented in terms of interbasin transitions between successive inherent structures without using the concept of intrabasin vibrations or normal modes [8,9]. This requires the analysis of a succession of multi-step interbasin transitions, not a one-step interbasin transition for short time interval. To the authors' knowledge, no one has attempted to examine such a possibility in molecular dynamics simulations probably because of heavy computational demands. Before challenging an ultimate problem of glass-formation, an essential subject at the present stage is to clarify how the real particle-motions can be related to the potential surfaces of the systems in this way. The present study has been devoted to this subject.

Two Coulomb systems, LiCl and 50(mol%)LiCl-50 KCl, are examined by means of the MD simulations and relevant analyses of Stillinger's inherent structures, because it is known that they exhibit the following contrasting properties in experiments. First, no pure alkali halides such as LiCl and KCl can be cooled into the glassy state in experiments, whereas mixing of several components strengthens the glass-forming ability; for example, mixture 55 LiCl-32 KCl-8 CsCl-5 $BaCl_2$ (simply modeled as 50 LiCl-50 KCl in the present work) can be cooled into the glass [10]. Secondly, the mixed salts such as LiCl-KCl do exhibit the lowering of the cation diffusion relative to LiCl, as is known as Chemla's effect [11].

We emphasize that the present study is a first attempt to clarify the relationship between the real *diffusive* dynamics and the relevant potential minima. In particular, it is of importance to choose typical Coulomb systems as the research target, because most of the real glass-forming materials are Coulomb or ionic substances. Actually, Rose *et al.*, have already studied inherent structures of $(KCl)_{32}$ cluster [12]. However, there has so far been no exploration of inherent structures of ionic glass-forming bulk materials.

Section 2 describes the finite-temperature trajectory calculations based on MD simulations and the method of exploration of inherent structures. The results of thermodynamic and various dynamical properties are given and discussed in Sec. 3. Finally the conclusions are summarized in Sec. 4.

2 METHODS

2.1 *Finite-temperature MD Calculation*

The interionic potential function used in the MD simulations is of the following Born-Huggins-Mayer type:

$$\phi_{ij}(r) = z_i z_j e^2 r^{-1} + b_{ij}\exp((\sigma_{ij} - r)\rho_{ij}^{-1}) - d_{ij}r^{-6} - h_{ij}r^{-8}, \tag{1}$$

where the parameters z_i and z_j are the ionic formal charges, ± 1. This potential function represents the typically ionic interaction in terms of a sum of Coulombic, Born-type repulsion, and dispersion forces. Most of the parameters in the potential function were cited from Tosi and Fumi's ones [13] which have been extensively used in the previous simulation studies [5, 14, 15]. The used parameter values are given in Table 1 of Ref. 5, but some of them were replaced by $\rho_{\mathrm{Cl-Cl}} = 0.340$ Å, $d_{\mathrm{Cl-Cl}} = 117.6 \times 10^{-19}$ J Å^6, and $h_{\mathrm{Cl-Cl}} = 236.1 \times 10^{-19}$ J Å^8 in the present calculations.

Following Andersen and Nosé's technique [17], first isobaric-isothermal MD simulations have been carried out for the two alkali chlorides, LiCl and 50 LiCl-50 KCl, to obtain the trajectories at some finite temperatures. The procedure of the simulation is the same as that in our previous works [5, 14]. In the present study, the total number of ions was set to $N = 64$ for both systems (LiCl : $N_{\mathrm{Li}^+} = 32$ and $N_{\mathrm{Cl}^-} = 32$; LiCl-KCl: $N_{\mathrm{Li}^+} = 16, N_{\mathrm{K}^+} = 16$, and $N_{\mathrm{Cl}^-} = 32$). The external pressure was set at 1.013×10^8 Pa throughout the simulations. The Coulombic potentials were evaluated by using Ewald's method. The glassy state is achieved by cooling the liquids at the rate 5×10^{13} Ks^{-1}. The MD trajectory was obtained for three million steps (6 ns) each for 1200, 900, 600, and 300 K, and 50 000 steps (100 ps) for other temperatures. Relatively small number of ions ($N = 64$) is for the purpose to save the computational time necessary for the steepest-descent quenching described in the next section. We have also carried out the simulation of the $N = 512$ systems under the same external condition to confirm that there are no differences between the thermodynamic properties of $N = 512$ and 64 systems.

2.2. *Exploration of Inherent Structures*

Stillinger's inherent structures of each temperature were explored by quenching each MD configuration (each ionic coordinate and the system volume) of the $N = 64$ systems into the local potential minima [2]. For this purpose we solved the following equations representing the steepest-descent path:

$$m_i\dot{\mathbf{r}}_i = -\frac{\partial\Phi}{\partial\mathbf{r}_i},\ i = 1, 2, \ldots, N \tag{2.1}$$

$$W\dot{V} = -\frac{\partial\Phi}{\partial V}, \tag{2.2}$$

where m_i and $\mathbf{r}_i$ are the mass and the position of i-th ion, Φ is potential energy of the system, W is the mass of Andersen's piston, and V is volume of the system [18]. The second equation is needed for the isobaric system where the quenching of the system volume must be also performed. The *time* step for the integration of this set of equations was 2×10^{-16}s, and 50 000 steps were computed to obtain one quenched configuration $\mathbf{Q}(\mathbf{r}_1^{(Q)}, \mathbf{r}_2^{(Q)}, \ldots, \mathbf{r}_N^{(Q)}, V^{(Q)}; t)$ which corresponds to a starting MD configuration $\mathbf{R}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, V; t)$. Ewald's sum was also evaluated during the quenching procedure. Totally 3 800 MD configurations at ten temperatures of the two systems were quenched into the inherent structures. This required to compute 1.9 billion steps which amount to CPU time as long as 140 days in Hewlett-Packard Model 715 work station.

3 RESULTS AND DISCUSSIONS

3.1 Thermodynamic Properties

Figure 1 shows the plot of calculated enthalpy as a function of temperature. As was mentioned the previous papers [5, 14], the liquid-glass transition of both systems is

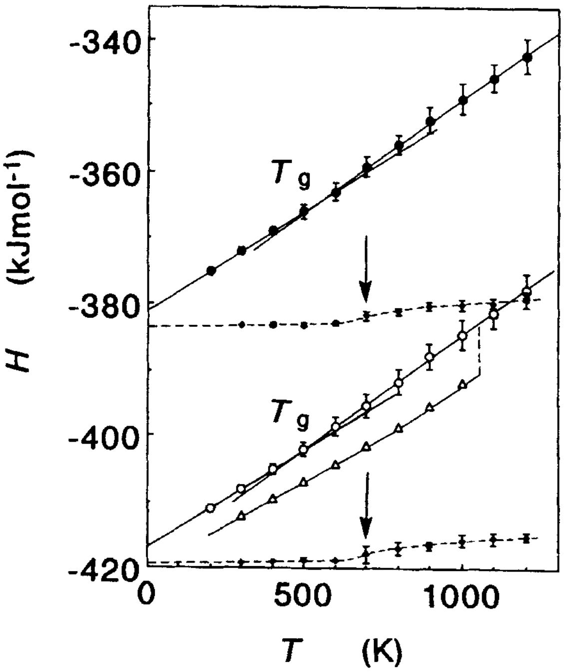


Figure 1 Plot of enthalpy as function of temperature. (–): H of real MD trajectory: (---): $H^{(Q)}$ of inherent structures. (Δ): crystalline LiCl; (○): liquid and glassy LiCl; (●): LiCl-KCl. The melting point of LiCl is found to be about 1100 K. Each $H^{(Q)}$ is an average of 50–300 quenched configurations. The standard deviations are shown as error bars except for the LiCl crystal. The arrows denote large fluctuation of $H^{(Q)}$ at 700 K.

recognized as a change of the H-T slopes or specific heat C_p at $T_g = 500-700$ K. The changes of C_p at T_g are 5.0 and 4.4 $\mathrm{JK^{-1}\,mol^{-1}}$ for the LiCl and LiCl-KCl systems, respectively. These are apparently much larger than experimental values of strong liquids such as $\mathrm{GeO_2}$(0.1 $\mathrm{JK^{-1}\,mol^{-1}}$) and $\mathrm{BeF_2}$(0.0 $\mathrm{JK^{-1}\,mol^{-1}}$) [19].

For inherent structures, we plotted in this figure *potential enthalpy* [18]

$$H^{(Q)} = \Phi^{(Q)} + P^{(Q)}V^{(Q)} \tag{3}$$

where $\Phi^{(Q)}, P^{(Q)}$, and $V^{(Q)}$ are the potential energy, system pressure, and volume averaged over 50–300 quenched inherent structures Q's. As for $H^{(Q)}$, the contribution of $P^{(Q)}V^{(Q)}$ is always negative ($-1.4 \sim -1.9$ $\mathrm{kJmol^{-1}}$) because of negative pressure for inherent structures. For both systems, there exists so significant enthalpic change at $T = 600-800$ K that the glassy and supercooled liquid states are well distinguished, as was expected previously [1]. Actually, the $H^{(Q)}$ gap between $T = 300$ K (glass) and 1200 K (liquid) is 3.9 and 4.5 $\mathrm{kJmol^{-1}}$ in LiCl and LiCl-KCl, respectively. The large energy-gap at T_g is characteristic of two-level systems accompanied with Schottky type specific heat [1]. In fact, the fluctuation or standard deviation of $H^{(Q)}$ is especially large at 700 K (1.3 and 0.7 $\mathrm{kJmol^{-1}}$ in LiCl and LiCl-KCl). Since the enthalpy of quenched systems essentially does not include thermal excitation on potential surfaces, this certainly implies the distribution of distinct configurations Q's at this temperature. Therefore, the number of configurations contributing to configurational entropy is remarkably excited at this temperature with heating. Further, these large energy gaps are also the evidences that both systems are classified into fragile liquids.

3.2 Dynamical Properties

Figure 2 shows the mean square displacements (MSD's) of the $\mathrm{Li^+}$ ions. We show two types of MSD's which were calculated from real MD trajectory,

$$M(t) = \frac{1}{N_{\mathrm{Li}}} \sum_{i \in \mathrm{Li}}^{N_{\mathrm{Li}}} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle, \tag{4.1}$$

and from inherent structures,

$$M^{(Q)}(t) = \frac{1}{N_{\mathrm{Li}}} \sum_{i \in \mathrm{Li}}^{N_{\mathrm{Li}}} \langle |\mathbf{r}_i^{(Q)}(t) - \mathbf{r}_i^{(Q)}(0)|^2 \rangle. \tag{4.2}$$

As for real dynamics $M(t)$ (Fig.2(a)), we can recognize regular diffusion ($M(t) \sim t$) for $t > 0.1$ ps at 1200 and 900 K and for $t > 100$ ps at 600 K. For 300 K (glass), however, there is not regular Brownian diffusion but so-called anomalous diffusion ($\sim t^{\alpha}, 0 < \alpha < 1$) [20] for all t. As for the difference between the two systems, at 1200 and 900 K ($> T_g$) faster diffusion of the $\mathrm{Li^+}$ ions in LiCl is recognized clearly than in LiCl-KCl. This manifests Chemla's effect that the diffusion of the $\mathrm{Li^+}$ ions is slowed down by mixing cation species [11]. It should be, however, mentioned that an inversion phenomenon is observed for 600 K ($\sim T_g$) and 300 K (glass), at which the $\mathrm{Li^+}$ ions in LiCl-KCl diffuse faster than in LiCl. It is emphasized that this fact has never been reported so far. We confirmed that these features in Figure 2(a) still hold in the $N = 512$ systems.

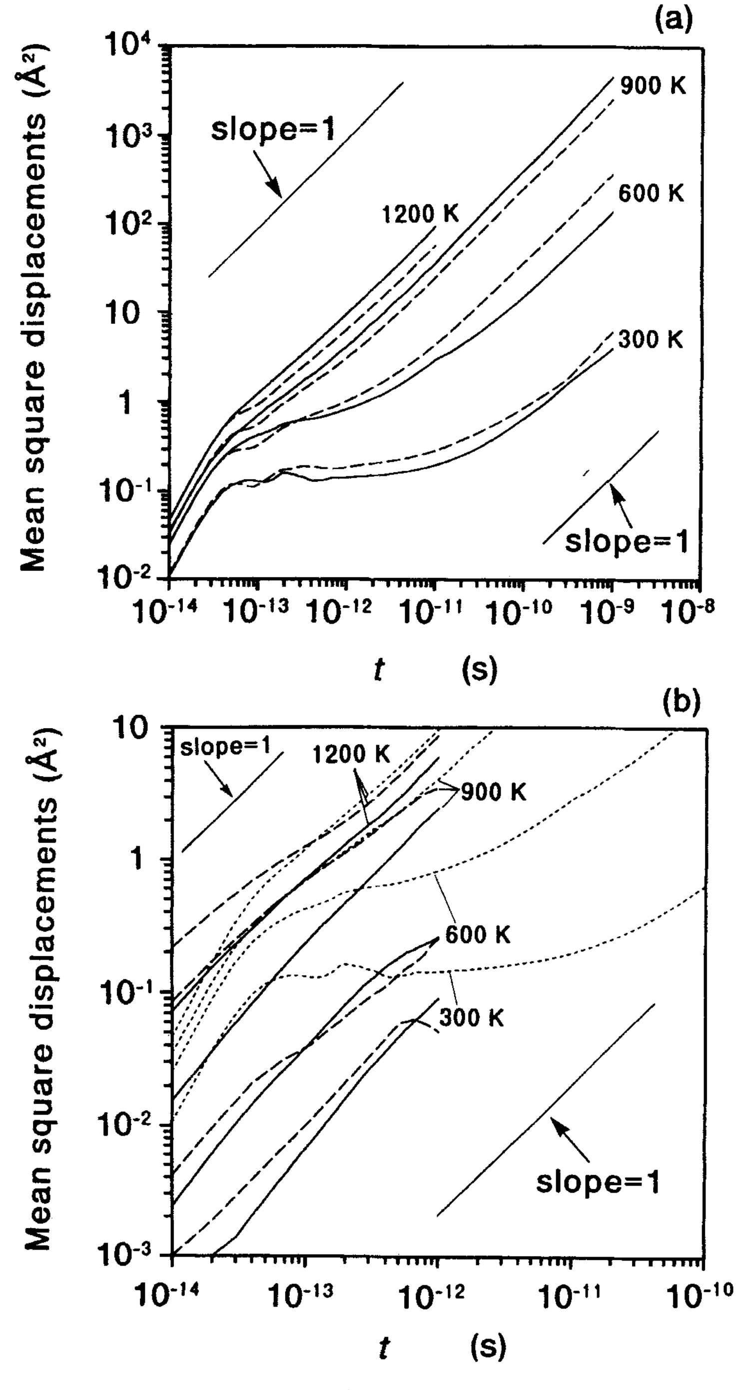


Figure 2 Mean square displacements of the Li^+ ions. (a) For real MD trajectory; (–): LiCl; (----): LiCl-KCl. (b) For inherent structures; (---): LiCl in real MD trajectory plotted for comparison; (– –): LiCl in inherent structures; (–): LiCl-KCl in inherent structures. Each $M^{(Q)}(t)$ is an average of 200–299 quenched configurations.

In Figure 2(b), the inherent structure MSD $M^{(Q)}(t)$ coincides well with $M(t)$ for $t > 0.1$ ps. Moreover, it is noteworthy that $M^{(Q)}(t)$ is almost Brownian ($\sim t$) even at very early time $t = 0.01$ ps, at 1200 and 900 K in LiCl. This clearly denotes that the interbasin transition process is completely free from vibrational motions and can represent the real diffusive motions at these temperatures. Moreover, we can see that Chemla's effect and the inversion phenomenon are almost conserved in $M^{(Q)}(t)$ at these temperatures. At lower temperatures (600 and 300 K), it is observed that $M^{(Q)}(t)$ fairly deviates from $M(t)$. However, this should be attributed to statistical errors caused by decrease of large interbasin transitions at low temperatures. Thus, we can conclude that the interbasin transitions $M^{(Q)}(t)$ can realize the essential features observed in the real MD trajectory at least qualitatively.

Since diffusive processes can be described in terms of the interbasin transition at very short time $t = 0.01$ ps, as is seen in Figure 2, we can consider each interbasin transition during 0.01 pa as an elementary process of overall ionic diffusive motions. In Figure 3 are shown together the self-part of van Hove functions $G_s(r, t)$ at $t = 0.01$ ps calculated from real MD trajectory,

$$G_s(r, t = 0.01 \text{ ps}) = \frac{1}{N_{\text{Li}}}\left\langle \sum_{i \in \text{Li}}^{N_{\text{Li}}} \delta(r - |\mathbf{r}_i(t = 0.01 \text{ ps}) - \mathbf{r}_i(0)|)\right\rangle, \tag{5.1}$$

and from inherent structures,

$$G_s^{(Q)}(r, t = 0.01 \text{ ps}) = \frac{1}{N_{\text{Li}}}\left\langle \sum_{i \in \text{Li}}^{N_{\text{Li}}} \delta(r - |\mathbf{r}_i^{(Q)}(t = 0.01 \text{ ps}) - \mathbf{r}_i^{(Q)}(0)|)\right\rangle. \tag{5.2}$$

Van Hove function for real trajectory G_s simply denotes an amplitude of thermal vibration $< 0.5\,\text{Å}$ for such a short time, while $G_s^{(Q)}$ for inherent structures has a wide distribution at larger r. For example, there is a distribution even at $r = 3\,\text{Å}$ at 1200 K, because ions which were moving in saddle region of potential surface during 0.01 ps are quenched separately in the two neighboring local minima. It is surprising that there is such a displacement as large as interionic spacing [14]. This means that potential minima visited by the ions are occasionally so much separated spatially.

To see the details of this short-time transitions, we show in Figure 4 the average displacements of the Li^+ ions during 0.01 ps, defined as

$$\Delta R(t) = \frac{1}{N_{\text{Li}}} \sum_{i \in \text{Li}}^{N_{\text{Li}}} |\mathbf{r}_i(t + 0.01 \text{ ps}) - \mathbf{r}_i(t)|. \tag{6}$$

Similarly the average displacements $\Delta R^{(Q)}(t)$ for inherent structures are defined in terms of $\mathbf{r}_i^{(Q)}$. In Figure 4(a) and 4(b), $\Delta R(t)$ for real trajectory keeps almost a constant value because it only represents the vibrational amplitude for 0.01 ps. We have confirmed that this is also the case of the other temperatures, including glassy state. On the other hand, $\Delta R^{(Q)}(t)$ representing the interbasin transitions in inherent structures exhibits the occurrence of intermittent transitions whose displacements are sometimes larger than the vibrational amplitude. Of course, these findings in $\Delta R(t)$ and $\Delta R^{(Q)}(t)$ also correspond to those in van Hove functions $G_s(r, t)$ and $G_s^{(Q)}(r, t)$ in Figure 3. We emphasize that the interbasin transitions are intermittent events even at 900 K at which continuous regular diffusion occurs in real MD trajectory.

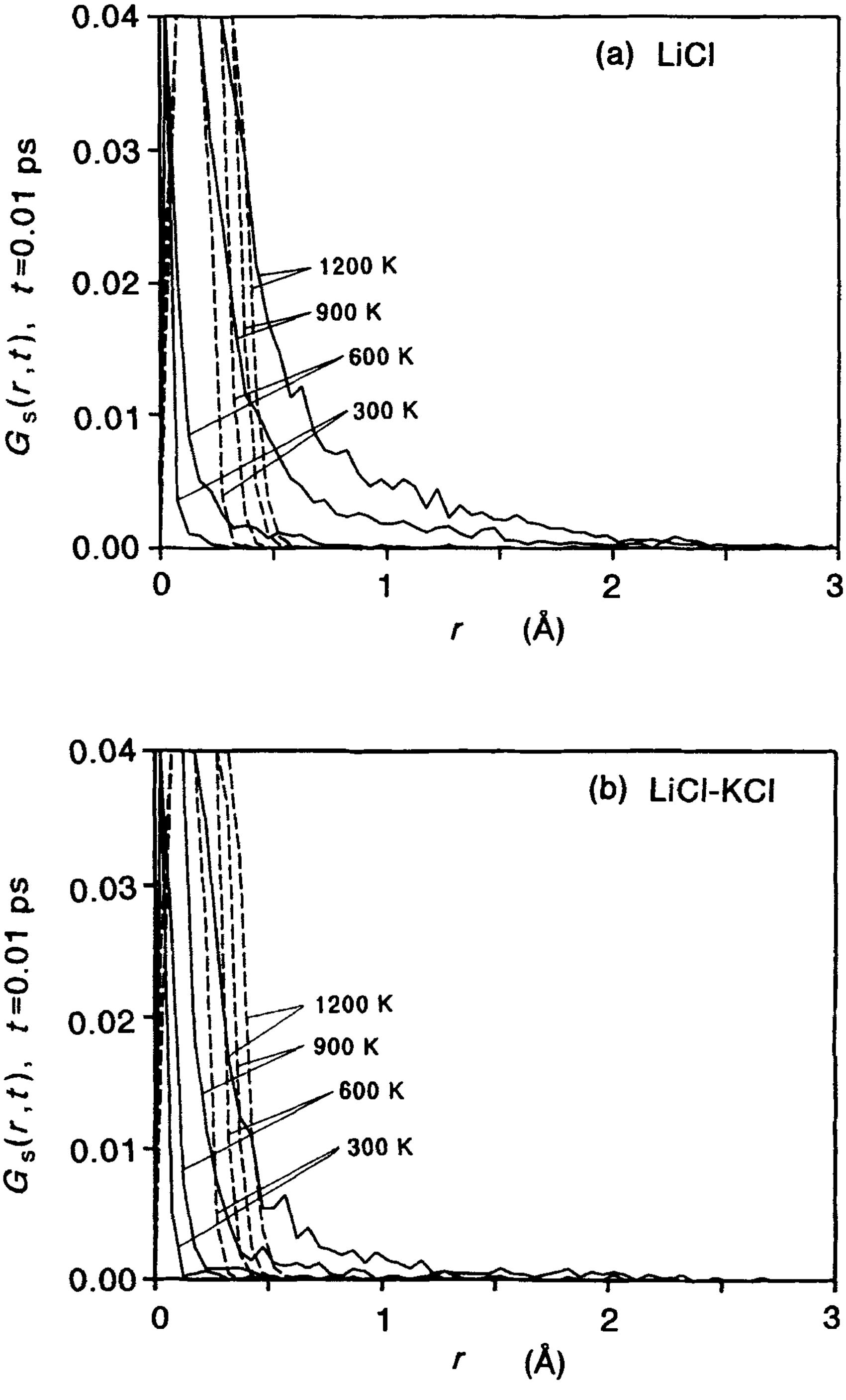


Figure 3 The self-part of van Hove functions of the Li^+ions for $t = 0.01$ ps. (---): $G_s(r, t)$ for real MD trajectory; (–): $G_s^{(Q)}(r, t)$ for inherent structues.

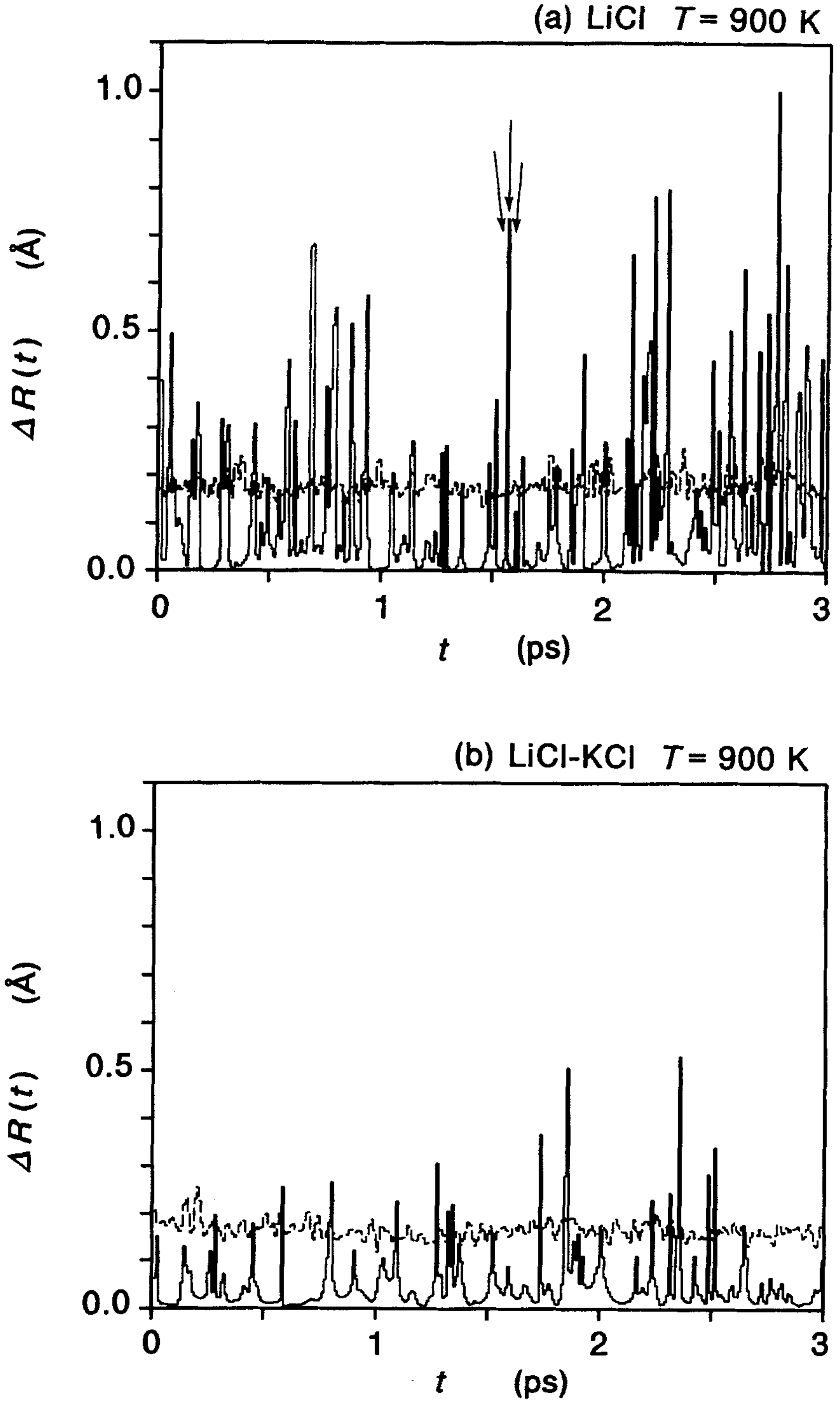
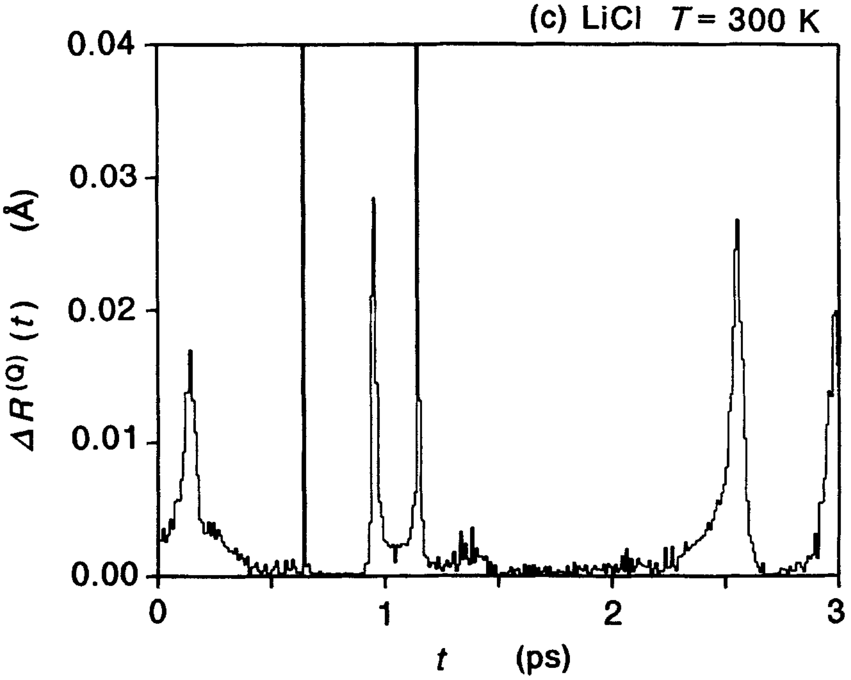
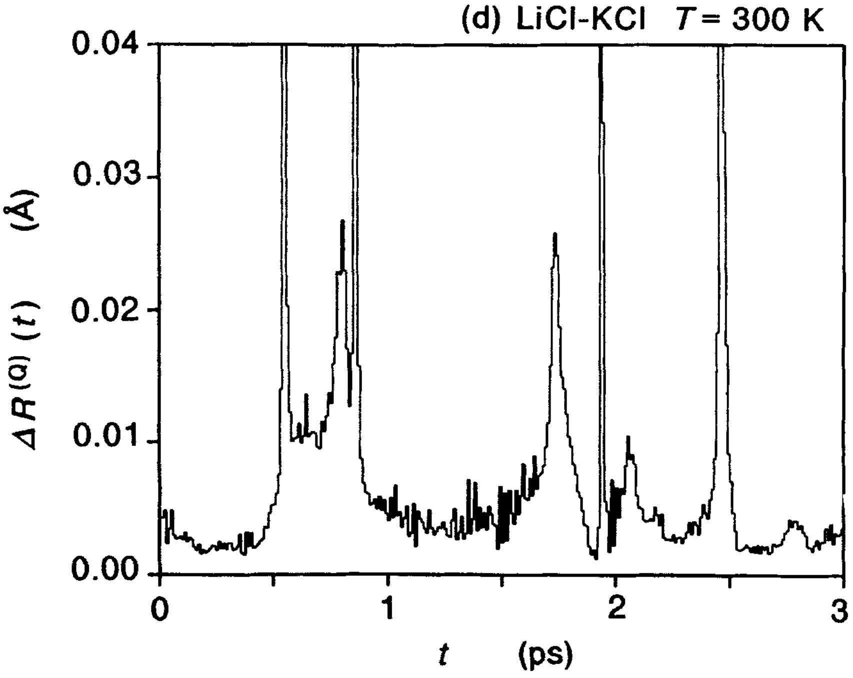

(a) LiCl T = 900 K
$\Delta R(t)$ (Å)
1.0
0.5
0.0
0
1
2
3
t (ps)
(b) LiCl-KCl T = 900 K
$\Delta R(t)$ (Å)
1.0
0.5
0.0
0
1
2
3
t (ps)

Figure 4



(c) LiCl $T = 300$ K



(d) LiCl-KCl $T = 300$ K

Figure 4 The average displacements of the Li^+ ions during 0.01 ps. (---): ΔR (t) for real MD trajectory; (–): $\Delta R^{(Q)}(t)$ for inherent structures. Note that the ordinate scale in (c) and (d) are extended from (a) and (b). The arrows in (a) denote the example of the spatial transitions shown in Figure 6.

In fact, the interbasin transitions $\Delta R^{(Q)}(t)$ are classified into three distinct patterns: (i) jump motions ($\Delta R^{(Q)} > 0.005$ Å), (ii) residual motions ($\Delta R^{(Q)} \leqslant 0.005$ Å), and (iii) residence in basin ($\Delta R^{(Q)} \sim 0$ Å). For example, in LiCl, at 900 K (Fig. 4(a)) frequent jump motions occur after and before residence in basins, while at 300 K (Fig. 4(c)) jump motions are more infrequent and the residence in basins becomes predominant. On the other hand, the displacement becomes small with decrease of temperature as well. For example, the largest displacement of jump motions in LiCl is $\Delta R^{(Q)} = 1.0$ Å at 900 K, while it is less than 0.2 Å at 300 K glassy state. Thus the lowering of temperature causes the decrease of both displacement and frequency of jump motions in inherent structures. Moreover, in LiCl-KCl at 900 K, both displacements and frequency of jumps are smaller than in LiCl (Fig. 4(a)(b)); this is in good agreement with the slower diffusion in LiCl-KCl at this temperature (Fig. 2).

Although the residence in basins is observed in LiCl at 300 K, the second type of transition, namely, the residual motions are remarkably observed in LiCl-KCl at 300 K (Fig. 4(d)). These residual motions are invisible and hidden under vibrational motions in the finite-temperature MD trajectory. Moreover, for $\Delta R^{(Q)}$ at 900 K as well (Fig. 4(b)), there are relatively small displacements which precedes and follows each prominent jump-type transition. This is in contrast to the LiCl liquid where each jump-type transition is a sudden event occurring just after residence without any precursory motions (Fig. 4(a)). Thus, the interbasin transitions in inherent structures of liquid and glassy LiCl-KCl exhibit a feature different from LiCl. Especially in the glassy state of LiCl-KCl, there exist slow structural relaxation due to these residual motions distinguished from jump motions.

As a result of these characteristics of both systems, patterns of the interbasin transition between each quenched configuration Q(t) can be viewed in contrast. Figure 5 shows the ionic transition patterns in the inherent structures of both glasses. We can see a significant system difference. For LiCl, the distinction between residence in basins and large jump-type transitions is clear. On the other hand, for

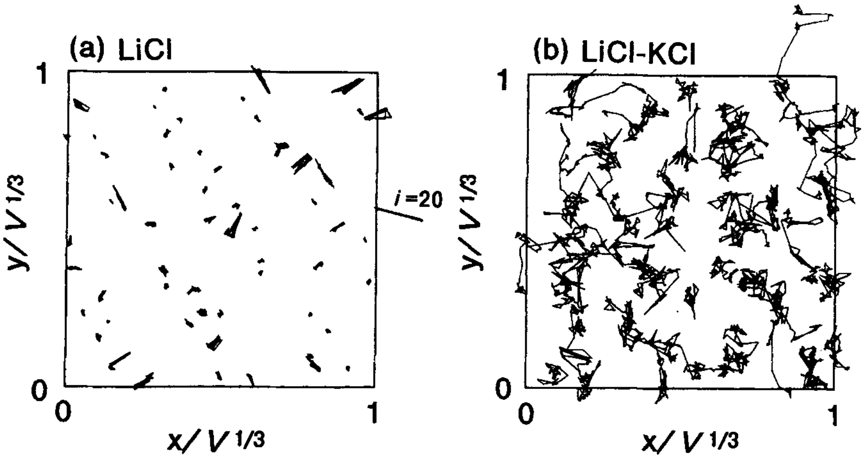


Figure 5 Patterns of the ionic transition between 100 successive inherent structures of the glasses at 300 K. Ionic positions at each 1 ps are connected by lines. The z-coordinate is projected onto the xy-plane of each simulation box.

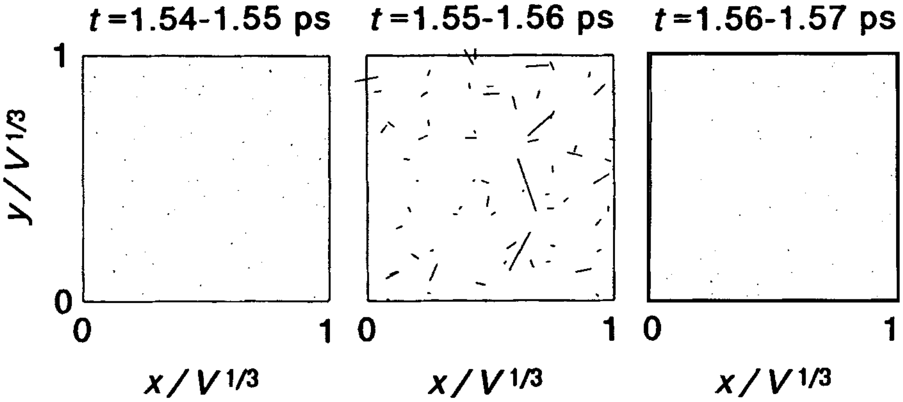


Figure 6 Patterns of the ionic transition between the successive inherent structures of LiCl at 900 K for $t = 1.54 - 1.57$ ps.

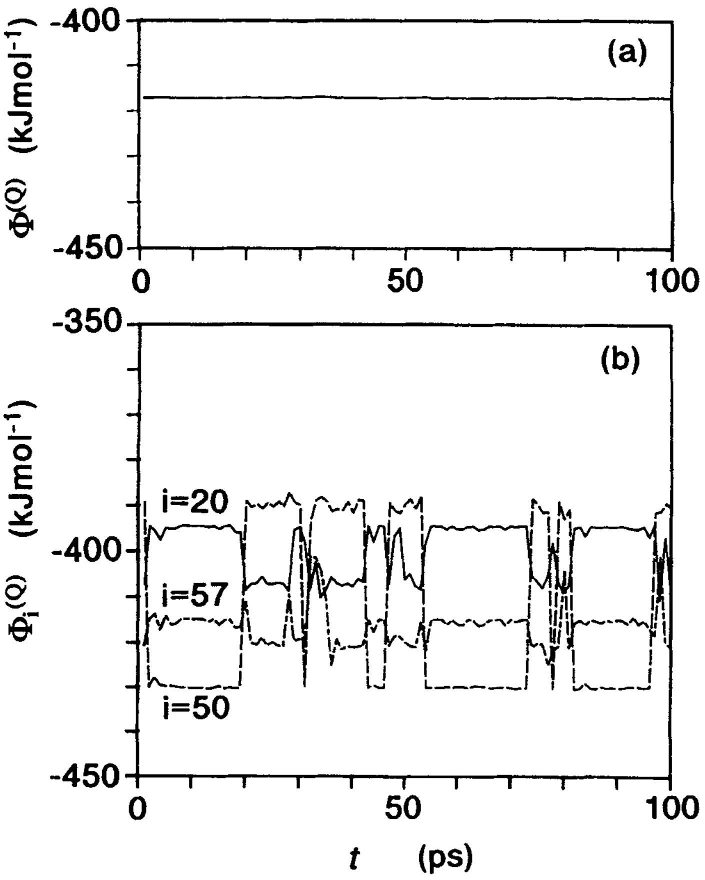


Figure 7 Total and some individual potential energies in inherent structures of LiCl at 300 K. (a) total potential energy $\Phi^{(Q)}$; (b) individual potential energy $\Phi_i^{(Q)}(i = 20\ (\mathrm{Li}^+),\ 50(\mathrm{Cl}^-)$, and $57\ (\mathrm{Cl}^-))$. $\Phi_i^{(Q)}$ is also calculated by means of Ewald's method, of course.

LiCl-KCl, the transition patterns are rather diffusive passing through various basin sites. These are in agreement with the findings in Figure 4.

Finally, we mention that jump-type transitions are, in principle, collective to which most of ions in the system participate. For example, the inherent structure transitions in LiCl at 900 K for $t = 1.54\text{-}1.57$ ps are shown in Figure 6. In this figure a succession of "residence→collective jump→residence" is clearly recognized; the jump occurs suddenly and the ions transit to the next basins collectively at the same moment. With such jump-type transitions, the individual potential energy of each ion,

$$\Phi_i^{(Q)} = \frac{1}{2}\sum_{j\neq i}^{N} \phi_{ij}(r_{ij}^{(Q)}), \tag{7}$$

actually changes as much as <40 kJmol^{-1}. For example, the time evolution of $\Phi_i^{(Q)}(t)$ in LiCl at 300 K is plotted in Figure 7(b). Each Φ_i changes discontinuously at the moment of interbasin jump-type transitions. However, the total potential energy $\Phi^{(Q)}$ does not alter so much as individual potential energy $\Phi_i^{(Q)}$ with time because the changes of each $\Phi_i^{(Q)}$ cancels out mutually (Fig. 7(a)). The fluctuation of $\Phi^{(Q)}$ is as small as the standard deviation shown in Figure 1 (*e.g.*, 0.02 kJmol^{-1} in LiCl at 300 K). This canceling out of $\Phi_i^{(Q)}$ is considered as a feature of Coulomb systems, where unbalanced local charge should be always neutralized by the displacements of distant ions through long-range Coulomb forces.

4 CONCLUSIONS

Stillinger's inherent structures, namely, the configurations of the quenched potential minima were explored for two Coulomb systems LiCl and LiCl-KCl. We have discussed the thermodynamic and single-particle dynamical properties especially on the basis of quenched inherent structures. As for the thermodynamic properties, we have found that there is an energy gap between the inherent structure enthalpies of the supercooled liquid and of glassy states. Furthermore, the fluctuation of the inherent structure enthalpy is fairly larger around the glass transition temperature. We have thus obtained a concrete evidence that LiCl and LiCl-KCl should be classified into *fragile* liquids in Angell's scheme.

For dynamical properties of real MD, Chemla's effect was observed for the temperatures at which regular diffusion is predominant, while an inverse phenomenon was observed for low temperatures at which anomalous diffusion is observed. On the other hand, the single-particle diffusion represented in MSD's proportional to t was successfully described as the successive interbasin transitions between inherent structures. In particular, the Brownian behavior in inherent structure dynamics is observed from very short time scale such as 0.01 ps though vibrational motions ($\sim t^2$) are predominant for such short time at finite temperatures. The interbasin transitions at every 0.01 ps are, however, intermittent even at high temperatures. The interbasin transitions are classified into three patterns; jump motions, residual motions, and residence in basins. All of them are hidden under vibrational motions in real MD trajectory. The mixture system LiCl-KCl include more prominent residual motions in the glassy state than LiCl.

We have concretely clarified the relationship between the finite-temperature ionic dynamics in real MD trajectory and the interbasin transitions in Stillinger's inherent structures. Although the coincidence of the real diffusion with the interbasin transition would have partly been predicted, we emphasize the significance that the present numerical results are the concrete evidences for this. Moreover, it has been shown some differences of dynamical properties between LiCl and LiCl-KCl at low temperature. They are, for example, an inverse Chemla's phenomenon and the prominent residual motions distinguished from jump-type transitions. Although the statistics is not necessarily good because of the limitation of computational ability, we believe that the essential conclusions of the present study are invariant qualitatively. A future subject on this line is certainly to investigate the long-time self-diffusion processes in inherent structures at low temperature. To explore numerous inherent configurations sufficient for such a study requires much more computational time than that of the present work. If this is possible, the jump probability can be accurately estimated from such numerical data with better statistics. In this case, it seems that a generalization of the dynamical lattice model [21] or the trapping diffusion model [22] based on the master equation is necessary to include a distribution of jump distances. This generalized model accompanied with accurate jump probability will describe the self-diffusion dynamics on potential surfaces more realistically; this is a future subject.

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