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Investigation on Single Ion Dynamics of Molten Alkali Chlorides by Molecular Dynamics Simulations

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Single ion dynamics of the two ionic species in each molten alkali chlorides at 1100 K have been studied with the molecular dynamics method through velocity auto-correlation functions. The self-diffusion coefficients of these ions have also been calculated from the time integral of the corresponding ionic velocity auto-correlation functions, which are in good agreement with the experimental values. For molten alkali chlorides, the ionic mass significantly affects the ionic dynamics. The self-diffusion coefficients of the light ions are larger than those of the heavy ones. In addition to the self-diffusion coefficients, velocity auto-correlation functions can provide a more intuitive description for the single-ion dynamics. For each melt, the velocity auto-correlation function of the light ions decays faster and exhibits a much more pronounced back scattering than its heavier partner. The velocity auto-correlation function of the light ions will be oscillatory if the mass difference of the two ionic species is significant. The oscillatory amplitude also increases as the mass difference increases.

Keywords: Single ionic dynamics, Velocity auto-correlation function, Self-diffusion coefficient, Oscillatory.

INTRODUCTION

Due to their highly interesting thermo-physical, chemical and electrical properties, molten salts play a significant role in many applications, such as molten salt reactor [1], coolant [2], electrolytes [3], nuclear waste treatment [4] and energy storage devices [5]. For these liquid materials, owing to the difficulties of corrosion, volatility and high temperature, experiments are often very difficult to perform and molecular dynamics simulations has appeared as a viable way for filling the gap in the data bases, which has been proved to be effective in investigating the performance of molten salts [6-13].

Alkali halide melts are a kind of simple dense ionic liquids. A detailed knowledge of structures and dynamic properties, including both single-ion motion and collective behaviour in molten alkali halides [14-19] has been investigated with Fumi-Tosi potential [20] through molecular dynamics method. Single-ion motion can be discussed through the velocity auto-correlation functions (VACF) and the self-diffusion coefficients D, while D is also related to VACF as Green-Kubo relation [21]. In addition, D can also be calculated from mean-square displacement (MSD) as Einstein formula. For classical systems, the above-mentioned two methods are strictly equivalent in calculating self-diffusion coefficients [22]. However, in addition to the quantitative self-diffusion coefficients data, velocity auto-correlation functions can give much more information about the single ion dynamics.

Molecular dynamics results on single ion dynamics have also been available for some molten monovalent halides concerning with the differences in size and mass of the two ions, which have proved that the VACF of the lighter ion is oscillatory intensively when the mass difference is large. This phenomenon can be explained as a “rattling” motion of the lighter ion in the cage formed by the heavier neighbours and is especially marked for Li^+ ion [21]. Ciccotti and Jacucci [23] also reported that the VACF of one ion is strongly oscillatory if it is significantly smaller than its partner for molten LiF, RbCl and RbI. The size and mass dependences of single ion dynamics in molten RbCl, NaI, AgCl and CuCl [24] have also been studied intensively with velocity auto-correlation functions by approximate theoretical predictions and molecular simulations and conclusions were made that, for light ions, the difference in mass could promote its rattling motion, while for large ions, the difference in size could encourage its oscillatory back scattering.

Previous work mainly focused on collective properties or structures on molten alkali chlorides [19] and their mixtures [25]. A detailed computational test on the single ionic dynamics in molten alkali chlorides will be presented here.

EXPERIMENTAL

The velocity autocorrelation functions of molten alkali metal chlorides at 1100 K have been studied. The potential model and simulation details could refer to Wang *et al.* [19]. The VACF [21,22,26] is defined as follows:

$$C_V(t) = \langle v_{i\alpha}(0)\cdot v_{i\alpha}(t)\rangle \tag{1}$$

where $v_{i\alpha}$ is the velocity of ion α, angular brackets indicate ensemble average. Using the Green-Kubo relationship [21,22], the ionic self-diffusion coefficients D can be obtained from the time integral of the VACF in the steady state equilibrated molecular simulation (EMD) method:

$$D = \frac{1}{3}\int_0^\infty \langle v_i(0)\cdot v_i(t)\rangle dt \tag{2}$$

RESULTS AND DISCUSSION

To capture the decay of VACF and to ensure the stability of the corresponding running integral, the time to compute velocity auto-correlation function (VACF) should be long enough. Firstly, the decay and corresponding running integral performances of the VACFs for molten alkali metal chlorides were tested. The normalized VACFs of ions in molten ACl all decay to zero quickly within 1.0 ps for all systems. The corresponding running integrals also reach stability after some short time, shorter than 2 ps. Fig. 1 shows the normalized VACFs and the corresponding running integrals of Cs^+ and Cl^- ions in molten CsCl at 1100 K. Thus, a time of 5 ps has been used for the VACF calculations.

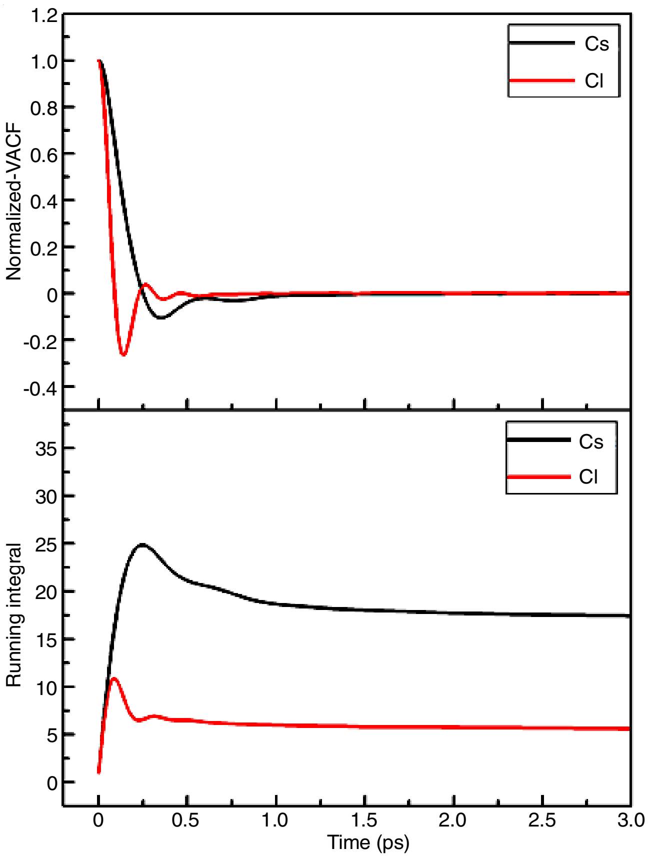

Fig. 1. Normalized velocity auto-correlation function and the corresponding running integral for Cs^+ and Cl^- ions in molten CsCl at 1100 K

The ionic self-diffusion coefficients of molten ACl at 1100 K calculated from the time integrals of the VACFs are listed and compared with the values obtained from the slope of the MSD as well as available experimental values [27,28] in Table-1.

TABLE-1
DIFFUSION COEFFICIENTS OF MOLTEN ACl AT 1100 K (IN UNITS OF 10^{-9} m^2/s)

System	VACF		MSD		Expt	
	A^+	Cl^-	A^+	Cl^-	A^+	Cl^-
LiCl	13.61	10.33	14.72	10.74	-	-
NaCl	7.99	7.39	9.36	8.14	8.74	6.60
KCl	8.06	8.29	8.27	8.49	8.38	8.60
RbCl	5.56	6.11	5.68	5.86	6.42	5.77
CsCl	5.80	6.57	5.13	6.02	5.93	6.61

The comparisons show that the VACF method underestimate the self-diffusion coefficients of molten LiCl, NaCl, KCl and overestimates those of molten CsCl than MSD method and the ionic self-diffusion coefficients of molten CsCl calculated from VACF method are in better agreement with the experimental values than those obtained from MSD method. For molten NaCl and RbCl, compared with the experimental values, the VACF method underestimates the cationic self-diffusion coefficients and overestimates the self-diffusion coefficients of the chloride ions. While for molten KCl and molten CsCl, the VACF method underestimates the self-diffusion coefficients of both two ionic species. However, the errors are below 5 %. In general, the self-diffusion coefficients calculated from the time integral of the ionic VACFs are in good agreement with the experimental tests. The results of molten LiCl at 1100 K herein are consistent with those calculated from the time integral of the VACF by Lantelme and Turq [29] at 1096 K, *i.e.*,

$$D(Li^+) = 12.46 \times 10^{-9}\ m^2/s$$
$$D(Cl^-) = 9.71 \times 10^{-9}\ m^2/s$$

In addition to giving the quantitative ionic self-diffusion coefficients, the ionic velocity autocorrelation functions can also provide a intuitive description for the ionic dynamics. The velocity autocorrelation functions of molten ACl systems at 1100 K have been calculated by molecular dynamics simulation. Fig. 2 shows the normalized VACFs of the two ionic species in each system as well as the VACFs of all the alkali metal ions for comparison.

At first sight, the normalized VACFs of light ions decay more quickly and exhibit a more pronounced backscattering than those of the heavy ones in each melt and from Li ions to Cs ions, the decay rate of the normalized VACFs decreased gradually. In molten LiCl, as Li^+ is significantly smaller and lighter than Cl^-, the velocity auto-correlation function of Li ions is strongly oscillatory compared with that of Cl^- while the VACF of Cl ions only shows a weak backscattering. Although the VACF of Na^+ is also oscillatory compared with that of its partner Cl^-, the oscillatory amplitude of the VACF of Na^+ is smaller than that of Li^+, which may be due to its increasing mass and size. For KCl, in which the two ions are approximately equal in mass, the ionic velocity auto-correlation functions resemble in each other. For molten RbCl and

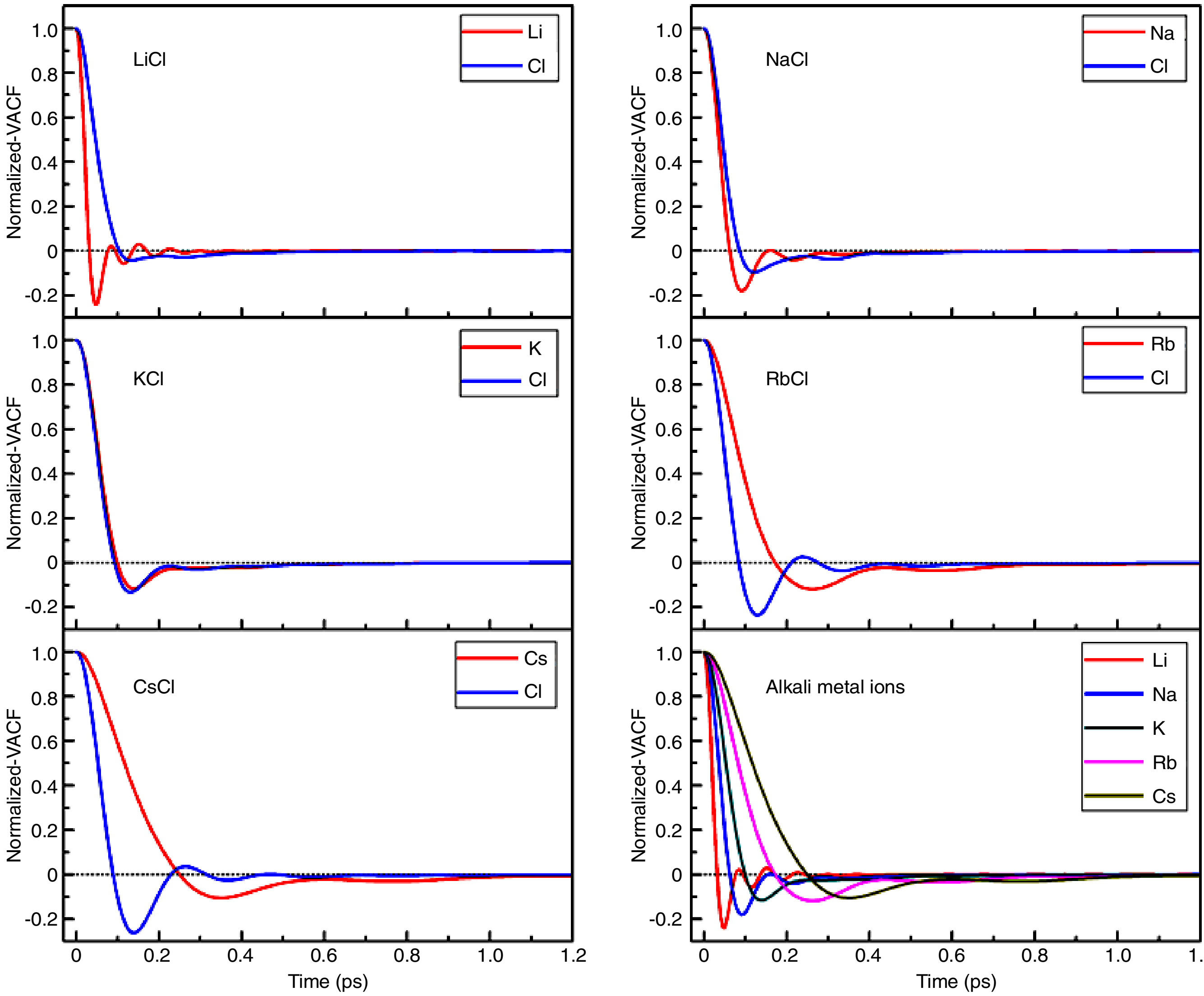

Fig. 2. Normalized velocity auto-correlation functions for molten ACl systems at 1100 K

CsCl, the VACFs of Cl⁻ become oscillatory, instead of a weak back scattering as in the cases of molten LiCl and NaCl. Although the ionic sizes are similar in molten RbCl, the velocity auto-correlation function of the lighter ions Cl⁻ is oscillatory compared with the VACF of Rb⁺. Conclusion can be made that it is the ionic mass rather than the ionic size that determined the single-ion dynamics for molten alkali chlorides systems.

In a certain system for molten alkali chlorides, the self-diffusion coefficient of the light ions is larger than that of the heavy ions, which indicates that the lighter ions has better locomotivity. Analysis from the shape of ionic velocity auto-correlation functions, that the VACFs of the light ions are more oscillatory and decay faster compared with those of the heavy ones, indicates that the light ions experience a "rattling" motion in the cage formed by its heavier neighbors of opposite charge [24].

Conclusion

The velocity auto-correlation functions (VACF) of the two ionic species in each molten alkali chlorides at 1100 K have been calculated by molecular dynamics simulations, which can be used to characterize the single ion dynamics. In addition to calculating the self-diffusion coefficients, the velocity auto-correlation functions can also provide a intuitive description for the ionic dynamics. The self diffusion coefficients calculated from the VACFs are in good agreement with experimental data and those values obtained from the mean square displacements. For a given molten alkali chloride, the ionic mass plays an important role on the ionic dynamics. The self-diffusion coefficient of the light ions is larger than that of the heavy ones. Likewise, the velocity auto-correlation function of the light ions decays more quickly than that of its partner. And the VACF of the light ions is oscillatory compared with that of its partner if the mass difference of the two ionic species is large enough, the oscillatory amplitude increases as the mass difference increases. For molten KCl in which the two species are nearly same in the mass, the ionic VACFs act similar to each other.

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REFERENCES

1. C. Le Brun, *J. Nucl. Mater.*, **360**, 1 (2007).
2. M.M. Waldrop, *Nature*, **492**, 26 (2012).
3. H. Groult, A. Barhoun, E. Briot, F. Lantelme and C.M. Julien, *J. Fluor. Chem.*, **132**, 1122 (2011).
4. K. Fukasawa, A. Uehara, T. Nagai, N. Sato, T. Fujii and H. Yamana, *J. Nucl. Mater.*, **424**, 17 (2012).
5. D.J. Bradwell, H. Kim, A.H. Sirk and D.R. Sadoway, *J. Am. Chem. Soc.*, **134**, 1895 (2012).
6. J. Trullas, O. Alcaraz, L.E. Gonzalez and M. Silbert, *J. Phys. Chem. B*, **107**, 282 (2003).
7. S.M. Urahata and M.C. Ribeiro, *Phys. Chem. Chem. Phys.*, **5**, 2619 (2003).
8. V. Bitrian and J. Trullas, *J. Phys. Chem. B*, **110**, 7490 (2006).
9. Y. Okamoto, S. Suzuki, H. Shiwaku, A. Ikeda-Ohno, T. Yaita and P.A. Madden, *J. Phys. Chem. A*, **114**, 4664 (2010).
10. O. Pauvert, M. Salanne, D. Zanghi, C. Simon, S. Reguer, D. Thiaudière, Y. Okamoto, H. Matsuura and C. Bessada, *J. Phys. Chem. B*, **115**, 9160 (2011).
11. M. Salanne, C. Simon, P. Turq and P.A. Madden, *J. Fluor. Chem.*, **130**, 38 (2009).
12. M. Levesque, V. Sarou-Kanian, M. Salanne, M. Gobet, H. Groult, C. Bessada, P.A. Madden and A.L. Rollet, *J. Chem. Phys.*, **138**, 184503 (2013).
13. V. Sarou-Kanian, A.L. Rollet, M. Salanne, C. Simon, C. Bessada and P.A. Madden, *Phys. Chem. Chem. Phys.*, **11**, 11501 (2009).
14. M. Dixon and J.M. Gillan, *Philos. Mag. Part B*, **43**, 1099 (1981).
15. N. Galamba, C.A. Nieto de Castro and J.F. Ely, *J. Chem. Phys.*, **120**, 8676 (2004).
16. N. Galamba, C. A. Nieto de Castro and J.F. Ely, *J. Chem. Phys.*, **122**, 224501 (2005).
17. D. Nevins and F.J. Spera, *Mol. Simul.*, **33**, 1261 (2007).
18. N. Ohtori, M. Salanne and P.A. Madden, *J. Chem. Phys.*, **130**, 1 (2009).
19. J. Wang, Z. Sun, G. Lu and J. Yu, *J. Phys. Chem. B*, **118**, 10196 (2014).
20. F.G. Fumi and M.P. Tosi, *J. Phys. Chem. Solids*, **25**, 31 (1964); M.P. Tosi and F.G. Fumi, *J. Phys. Chem. Solids*, **25**, 45 (1964).
21. J.P. Hansen and I.R. McDonald, Theory of Simple Liquids, Academic Press: London, edn 3 (2005).
22. D. Frenkel and B. Smit, Understanding Molecular Simulation-From Algorithms to Applications, Academic Press (1996).
23. G. Ciccotti, G. Jacucci and I.R. McDonald, *Phys. Rev. A*, **13**, 426 (1976).
24. O. Alcaraz and J. Trullas, *J. Chem. Phys.*, **113**, 10635 (2000).
25. J. Wang, J. Wu, Z. Sun, G. Lu and J. Yu, *J. Mol. Liq.*, **209**, 498 (2015).
26. M.P. Allen and D.J. Tlldesley, Computer Simulation of Liquids, Oxford University Press: Oxford, U.K. (1987).
27. J.M. Bockris and G.W. Hooper, *Discuss. Faraday Soc.*, **32**, 218 (1961).
28. J.O.M. Bockris, S.R. Richards and L. Nanis, *J. Phys. Chem.*, **69**, 1627 (1965).
29. F. Lantelme and P. Turq, *J. Chem. Phys.*, **77**, 3177 (1982).