Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information: Structure and Dynamics of the Molten Alkali-Chloride Salts from an X-ray, Simulation, and Rate Theory Perspective

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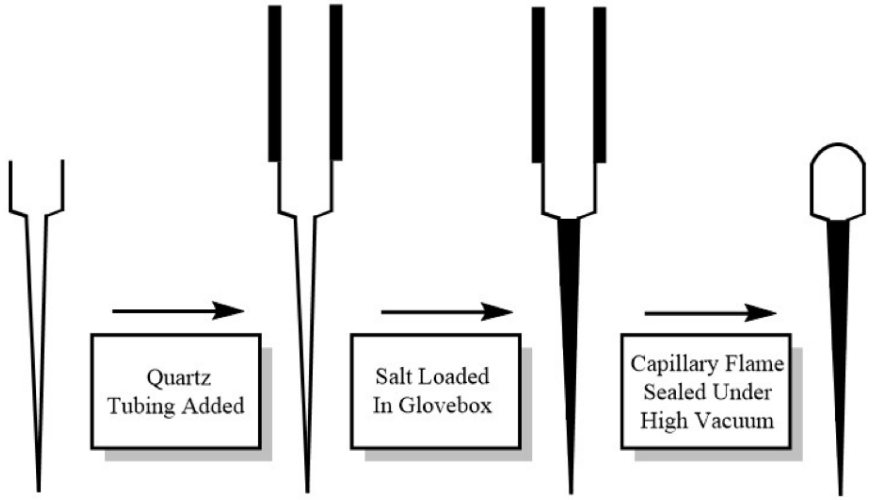

Figure S1: Procedure for packing capillaries.

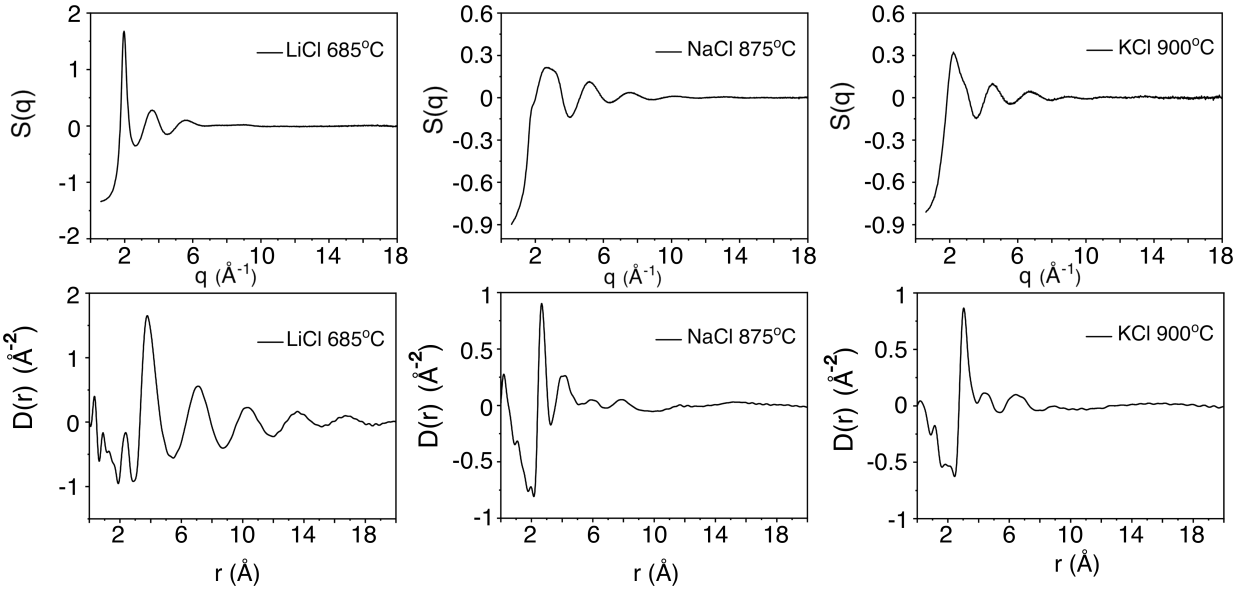

Figure S2: Experimental $S(q)$ and $D(r)$ functions displayed in their full q and r range.

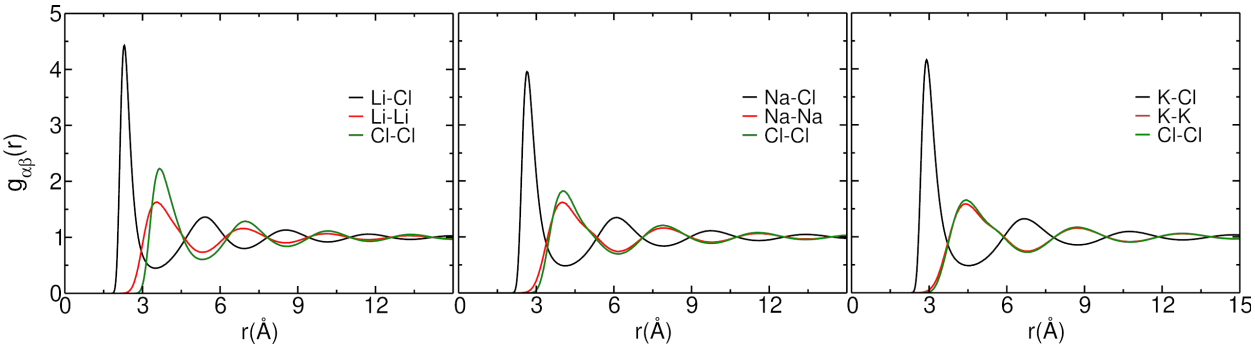

Figure S3: Radial distribution functions, $g_{\alpha\beta}(r)$, derived from our PIM simulations for LiCl at 958 K (left), NaCl at 1148 K (middle), and KCl at 1173 K (right).

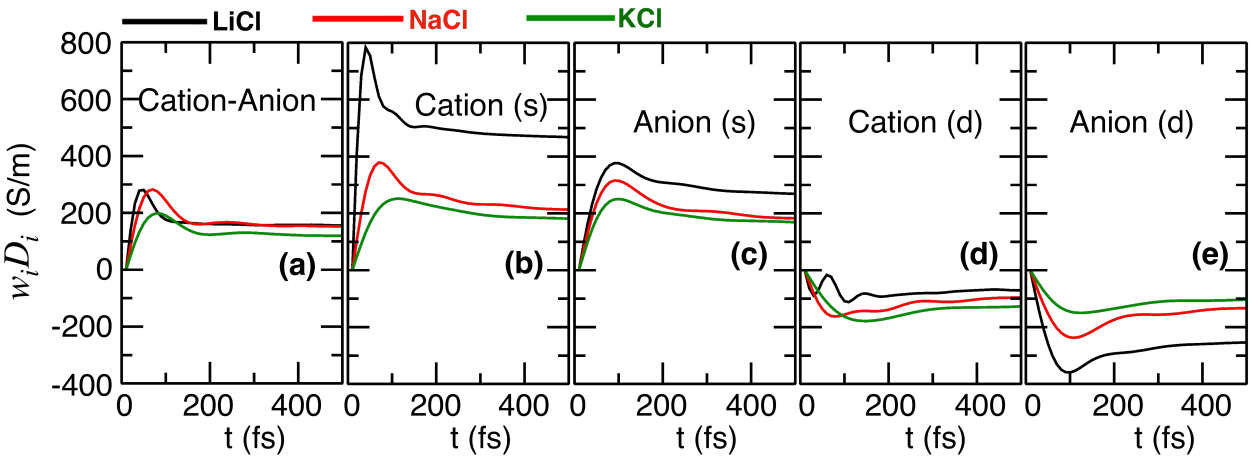

Figure S4: The time-dependent weighted contribution of the different diffusion coefficients to the conductivity, highlighting their short-time behavior.

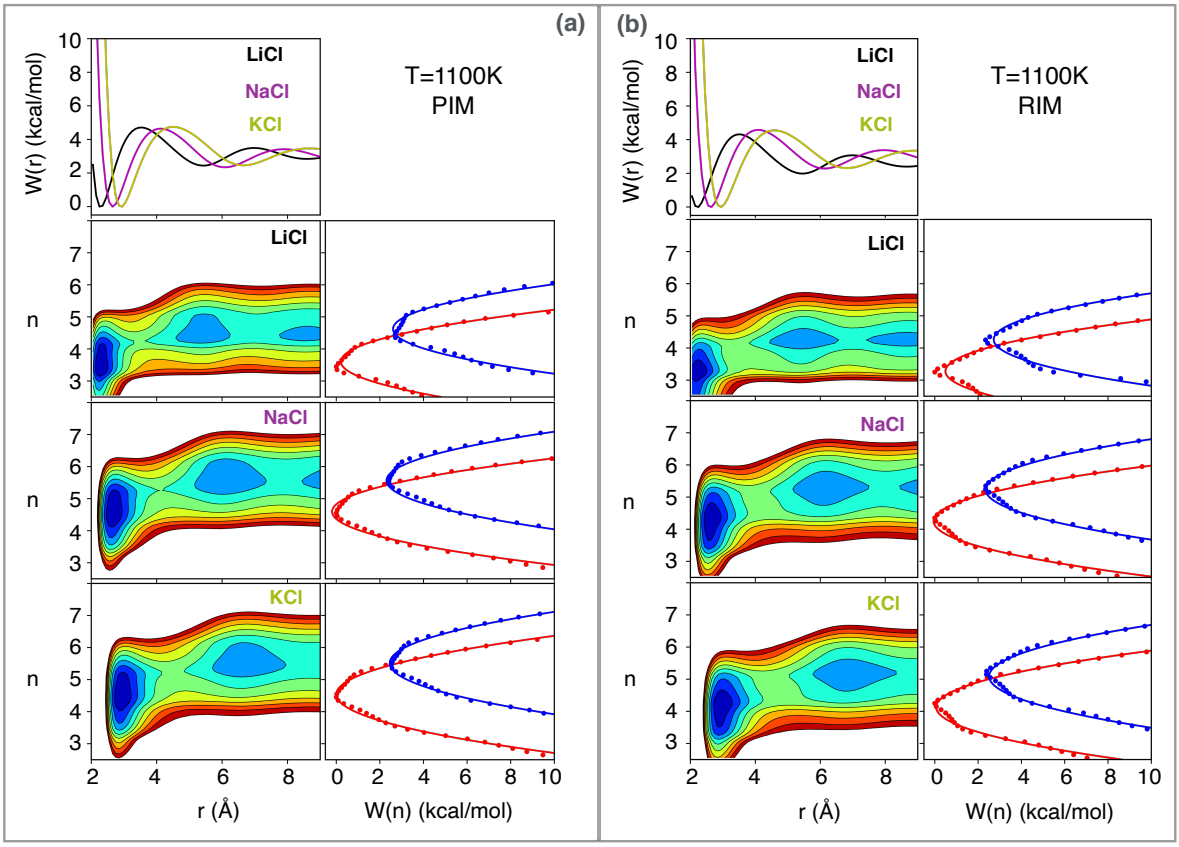

Figure S5: $W(r)$, $W(r,n)$, and $W(n)$ computed from PIM and RIM simulations at 1100 K. Contours are evenly spaced (1 kcal/mol) between 0 and 10 kcal/mol.

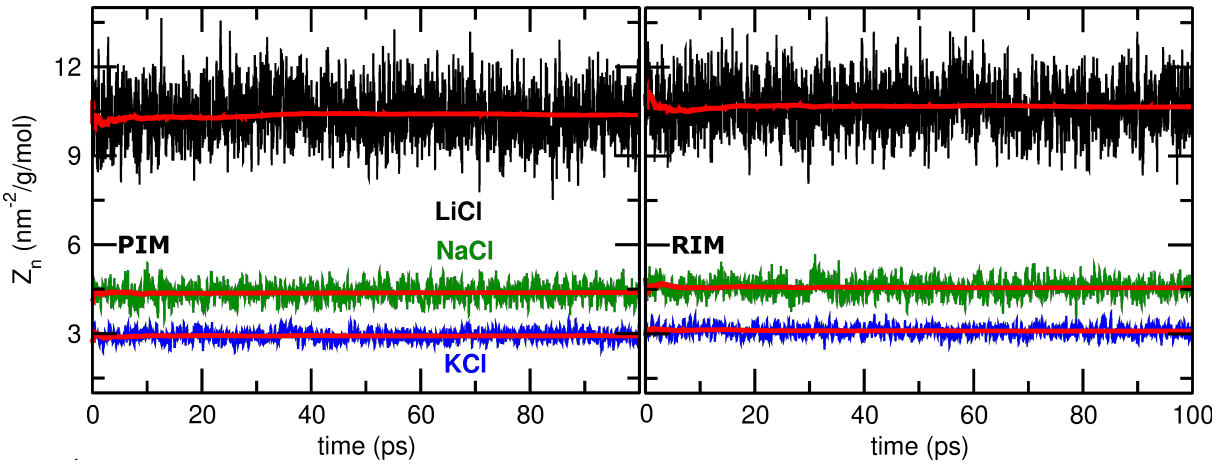

Figure S6: Z_n averaged over all possible ion pairs cases. We see that Z_n is for all practical purposes a conserved quantity that minimally fluctuates over time around its average value. All results are at 1100 K, and red lines are running averages.

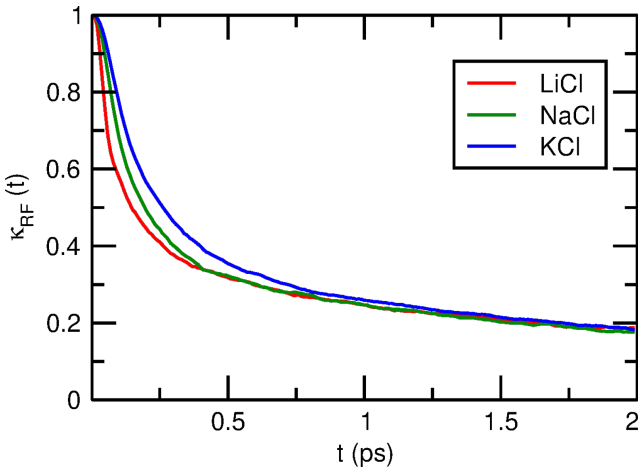

Figure S7: Reactive flux transmission coefficients obtained from RIM simulations at 1100 K.

Table S1: Cationic self-diffusion coefficient ($D^{\mathrm{S}}_{\mathrm{cat}}$), anion self-diffusion coefficient ($D^{\mathrm{S}}_{\mathrm{an}}$), ionic conductivity ($\sigma$), and molar ionic conductivity (σ_{M}), calculated from our RIM and PIM simulations at 1100K, compared with experimental data.[1,2]

	LiCl	NaCl	KCl
PIM			
$D^{\mathrm{S}}_{\mathrm{cat}}$ (10^{-4}cm^2/s)	1.441±0.019	0.887±0.017	0.852±0.014
$D^{\mathrm{S}}_{\mathrm{an}}$ (10^{-4}cm^2/s)	0.797±0.013	0.706±0.011	0.817±0.013
σ (S/m)	565.6±10.8	349.1±5.1	235.0±4.9
σ_{M} (S cm^2/mol)	167.6±3.2	114.3±1.9	117.0±2.4
RIM			
$D^{\mathrm{S}}_{\mathrm{cat}}$ (10^{-4}cm^2/s)	1.439±0.022	0.882±0.037	0.917±0.015
$D^{\mathrm{S}}_{\mathrm{an}}$ (10^{-4}cm^2/s)	1.104±0.017	0.817±0.025	0.913±0.012
σ (S/m)	602.6±6.4	304.3±3.3	253.2±3.8
σ_{M} (S cm^2/mol)	193.0±2.1	140.1±1.3	139.1±2.1
Experiment			
$D^{\mathrm{S}}_{\mathrm{cat}}$ (10^{-4}cm^2/s)	1.726	0.801	0.773
$D^{\mathrm{S}}_{\mathrm{an}}$ (10^{-4}cm^2/s)	0.834	0.635	0.690
σ (S/m)	672.1	366.0	230.4
σ_{M} (S cm^2/mol)	202.2	138.8	114.9

Table S2: For the Marcus-TST rate theory approach based on the coordination number n as the reaction coordinate, parameters for the different salts based on our PIM and RIM simulations. Equilibrium locations (n_{R} and n_{P}), curvature of reactant and product parabolas (K_{R} and K_{P}), coupling parameter (C), slope difference ($S_2 - S_1$), and traversal velocity at the crossing point (v_n).

	LiCl	NaCl	KCl
PIM			
n_{R}	3.61	4.60	4.54
n_{P}	4.62	5.57	5.52
K_{R} (kcal/mol)	7.50	7.35	5.98
K_{P} (kcal/mol)	7.57	6.63	5.91
C (kcal/mol)	0.60	0.40	0.19
v_n (fs^{-1})	0.007	0.005	0.004
$S_2 - S_1$ (kcal/mol)	7.63	7.03	5.85
RIM			
n_{R}	3.28	4.25	4.13
n_{P}	4.26	5.24	5.10
K_{R} (kcal/mol)	7.31	6.75	6.44
K_{P} (kcal/mol)	7.01	6.26	5.84
C (kcal/mol)	0.53	0.37	0.22
v_n (fs^{-1})	0.005	0.004	0.003
$S_2 - S_1$ (kcal/mol)	7.17	6.59	6.12

References

(1) Janz, G.; Dampier, F. W.; Lakshminarayanan, G. R.; Lorenz, P. K.; Tomkins, R. P. T. *Natl. Bur. Stand.*; 1968.

(2) Janz, G. J.; Bansal, N. P. Molten Salts Data: Diffusion Coefficients in Single and Multi Component Salt Systems. *J. Phys. Chem. Ref. Data* 1982, **11**, 505–693.