
Freezing in Halide Salts

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The static criterion that the amplitude of the principal peak of the liquid structure factor has a constant value along the freezing line and the onset of freezing are studied from the structure factors and the static dielectric functions of halide salts interacting via the effective pair potentials through the hypernetted-chain approximation. It is observed that the criterion above is restricted to the effective charge difference. The critical value of plasma parameter at freezing is affected by the mobility and number concentration of anions and cations. The distribution of the value of the static dielectric function closest to the wave number axis in the negative region is also determined by the charge difference and the ordering of ions and related to the onset of freezing.

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1. Introduction

The freezing transition is an interesting issue in physics, and its theoretical prediction is also important in chemical engineering. The dynamic and the static scaling, and the freezing criteria have preoccupied many scientists ever since the works by Lindeman [1], and Hansen and Verlet [2] (HV). The melting rule by Lindeman predicts that the ratio of the root-mean square displacement and the average interparticle distance at melting line of the solid has a value of 0.15. The dynamical criterion for colloidal and a two-dimensional fluids proposed by Löwen et al.[3, 4] states that the ratio of the long-time and short-time diffusion coefficient has the universal value 0.1 along the freezing line. In addition, Pesché et al. [5, 6] have recently shown that the reduced long-time self diffusion coefficient and the static structure factor have a functional relation, $D_s^L/D_0 = f(S(k_0))$ for colloidal fluids. According to the static freezing criterion formulated by HV, the amplitude of the main peak in the static structure factor $S(k)$ at k_0 into which

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a neutral monatomic fluid freezes reaches a universal value between 2.8 and 3.1 near freezing [2, 7]. $S(k_0)$ has been found to be about 3.0 for alkali metals [8]. However, it reaches the value of 5.5 for two-dimensional liquid [5, 9], that leads to the violation of the HV freezing rule.

For a two-component liquid, the number and charge structure factors are the appropriate tools for the purpose of studying the freezing criterion. March and Tosi [10] (MT) have proposed a criterion for freezing of alkali halides by using the analogy with the classical one-component plasma (OCP), in which the freezing transition occurs at a critical value of the plasma parameter $\Gamma \cong 160-180$. At this critical value of the plasma parameter, the main peak height of the charge-charge structure factor $S_{QQ}(k_0)$ has the value of 2.7-3.1 [11-13]. The difference between cations and anions are ignored in a two-component system when the structure is described by number density ρ_N while the charge density ρ_Q is directly reflecting the ionic character of the structure. The $S_{QQ}(k)$ is generated by correlating the charge density fluctuations as $\langle \rho_Q(k)\rho_Q(-k) \rangle$ and reflects the residual short-range ordering in the ionic liquid. In contrast to the number-number and the number-charge structure factor, $S_{NN}(k)$ and $S_{NQ}(k)$, the $S_{QQ}(k)$ show a very prominent principal peak and qualitatively resemble the structure factor of an ordinary monatomic liquid just above the freezing point. This justifies the use of the $S_{QQ}(k)$ for the freezing criterion in alkali halides by MT. According to this criterion the amplitude of the principal peak in $S_{QQ}(k)$ has the constant value along the freezing line and was estimated to be $S_{QQ}(k_0) \approx 5$ from the available data, when extrapolated to the freezing point.

Another important concept of condensed matter physics is the dielectric function $\varepsilon(\mathbf{k}, \omega)$ which provides a direct measure of the dielectric response of the system. The behavior of the wave number-dependent static dielectric function $\varepsilon(k)$ is related to the freezing mechanism in ionic liquids [14, 15, 11] and it can be calculated directly from the static structure factor. The fluid will be stable against the formation of charge density waves if $\varepsilon(k) > 1$ and $\varepsilon(k) < 0$; and would approach the instability as the $\varepsilon(k)$ rises towards zero from negative region at the value of k_0 which corresponds to the principal peak in the static structure factor or to the reciprocal lattice vector of the solid into which the fluid freezes. The studies on the static dielectric function to understand the freezing phenomenon in halide salts have been mainly for AgI and NaCl, which can be taken as representative systems for superionic conductors (SIC) and ordinary solids, respectively. The $\varepsilon(k)$ of molten AgI resembles more closely that of classical one-component plasma near the fluid-solid transition than that of the simple molten salt, NaCl. This is taken as the reflection of the covalent nature of AgI and the liquid like picture of the superionic phase [14].

In this paper, an intensive study of the static freezing criterion and the freezing mechanism of halide salts using the hypernetted-chain (HNC) theory of liquids and some experimental data is presented. We explore the freezing criterion for two

component liquids by MT further by following similar arguments. Therefore, for the purpose of this work, we mainly focus on the height of the principal peak in $S_{QQ}(k)$ at k_0 . Moreover, the static dielectric function $\varepsilon(k)$ was investigated in order to have a general view of the freezing process and to catch the sight of the effect of the nature of the freezing process to the static scaling in salts.

2. Theory

The dielectric function can be expressed in terms of density response function $R(\mathbf{k}, \omega)$ in the form of [8]:

$$\frac{1}{\varepsilon(\mathbf{k}, \omega)} = 1 + \frac{4\pi e^2}{k^2} R(\mathbf{k}, \omega). \quad (1)$$

In the static limit $R(\mathbf{k}, \omega)$ is then related directly to the structure factor $S(k)$

TABLE
Parameters for the effective pair potentials given by Eqs. (5) and (6), melting temperatures T_m [K], input data densities n [ions/Å³] used in the HNC calculations, the chemical activity parameters χ_M , the plasma parameters Γ and the values of the charge-charge structure factors $S_{QQ}(k_0)$. Potential parameters are listed for each system as the first line is for cation-cation, the second is for anion-anion and the third line is for the unlike ion pairs. Unit of lengths are given in Å, and of energies in $e^2/\text{Å} = 14.399$ eV.

Salt	$T_m^{a,b}$	Z_-	σ_+	σ_-	$C_{\alpha\beta}$	$H_{\alpha\beta}$	$P_{\alpha\beta}$	χ_M^d	$n^{a,b}$	Γ	$S_{QQ}(k_0)$
TlBr ^e	732 (0.05)	0.7	1.45	1.99	0.0	9.58	0.0	1.56	0.0246	102	3.300
					9.1	62.3	2.19				
					0.0	26.3	1.10				
TlCl ^e	703 (0.05)	0.68	1.40	1.92	0.0	15.0	0.0	1.56	0.0271	110	3.338
					5.8	133	1.60				
					0.0	48.8	0.80				
TlI ^e	713 (0.16)	0.65	1.54	2.10	0.0	3.20	0.0	1.56	0.0210	99	2.983
					19.0	4719	3.08				
					0.0	97.9	1.54				
AgBr ^f	707 (0.05)	0.66	0.85	2.04	0.0	0.30	0.0	1.18	0.0354	119	3.445
					7.79	59.5	1.81				
					0.0	7.43	0.91				
AgCl ^f	728 (0.05)	0.68	0.81	1.96	0.0	0.25	0.0	1.18	0.0406	121	3.352
					6.01	48.9	1.60				
					0.0	6.12	0.80				
AgI ^g	831 (0.05)	0.6	0.81	1.95	0.0	0.02	0.0	1.18	0.0281	93	3.380
					6.93	446	2.35				
					0.0	107	1.17				
CuCl ^g	695 (0.05)	0.5	0.46	1.81	0.0	0.004	0.0	1.20	0.0402	126	3.154
					5.77	132	0.87				
					0.0	4.29	0.43				
CuBr ^g	761 (0.05)	0.48	0.46	1.96	0.0	0.005	0.0	1.20	0.0338	108	2.718
					9.03	185	1.04				
					0.0	5.99	0.52				
CuI ^g	861 (0.05)	0.6	0.46	2.20	0.0	0.01	0.0	1.20	0.0266	89	2.717
					6.93	339	2.35				
					0.0	13.0	1.17				

TABLE (cont.)

Salt	$T_m^{a,b}$	Z_-	σ_+	σ_-	$\rho_{\alpha\beta}$	$C_{\alpha\beta}$	$D_{\alpha\beta}$	$B_{\alpha\beta}$	χ_M^d	$n^{a,b}$	Γ	S_{QQ}
NaCl ^h	1074 (0.05)	1.0	0.99	1.81	0.33	0.07	0.04	0.069	0.40	0.0319	76	3.219
					0.33	5.03	10.1	0.601				
					0.27	0.49	0.60	0.052				
NaBr ⁱ	1023 (0.05)	1.0	1.17	1.72	0.34	0.07	0.04	0.018	0.40	0.0211	69	3.368
						8.50	19.5	0.011				
						0.61	0.82	0.015				
NaI ^j	935 (0.05)	1.0	1.17	1.91	0.39	0.07	0.04	0.018	0.40	0.0217	76	3.402
						17.0	47.7	0.011				
						0.83	1.34	0.015				
NaF ^h	1253 (0.05)	1.0	0.99	1.29	0.33	0.07	0.03	0.051	0.40	0.0556	78	3.375
					0.33	0.72	0.87	0.035				
					0.27	0.0	0.0	0.049				
KCl ^h	1043 (0.05)	1.0	1.37	1.81	0.33	1.06	1.04	0.252	0.35	0.0245	71	3.317
					0.33	5.40	10.8	0.033				
					0.27	2.08	3.17	0.018				
KBr ⁱ	1008 (0.05)	1.0	1.46	1.72	0.34	1.05	1.04	0.018	0.35	0.0211	70	3.524
						8.93	19.5	0.011				
						2.60	4.29	0.015				
KI ^j	958 (0.05)	1.0	1.46	1.91	0.36	1.05	1.04	0.018	0.35	0.0174	69	3.398
						17.5	49.0	0.011				
						3.55	6.76	0.015				
KF ^h	1129 (0.05)	1.0	1.37	1.29	0.33	1.06	1.04	0.246	0.35	0.0394	77	3.742
					0.33	0.81	0.95	0.003				
					0.27	0.0	0.0	0.019				
LiCl ⁱ	883 (0.05)	1.0	0.82	1.59	0.34	0.0	0.0	0.029	0.45	0.0421	101	3.570
						4.81	9.67	0.011				
						0.09	0.10	0.020				
LiI ^j	722 (0.05)	1.0	0.82	1.91	0.43	0.0	0.0	0.029	0.45	0.0279	101	3.610
						16.4	46.0	0.011				
						0.14	0.23	0.020				
LiF ⁱ	1118 (0.05)	1.0	0.82	1.80	0.30	0.0	0.0	0.029	0.45	0.0828	100	3.134
						0.63	0.74	0.011				
						0.03	0.03	0.020				
RbCl ⁱ	988 (0.05)	1.0	1.59	1.56	0.32	2.58	3.56	0.018	0.30	0.0220	73	3.481
						5.64	11.3	0.011				
						3.43	5.81	0.015				
RbBr ⁱ	953 (0.05)	1.0	1.59	1.72	0.34	2.58	3.56	0.018	0.30	0.0194	72	3.616
						9.32	21.2	0.011				
						4.29	7.80	0.015				
RbI ^j	913 (0.05)	1.0	1.59	1.91	0.34	2.58	3.56	0.018	0.30	0.0162	71	3.579
						18.6	52.0	0.011				
						5.85	12.1	0.015				

through the classical form of the fluctuation-dissipation theorem,

$$R(k) = -(n/k_B T)S(k). \quad (2)$$

Finally, $\varepsilon(k)$ is written for an ionic fluid system provided that $S(k)$ is interpreted as correlation function between charge density fluctuations, $S_{QQ}(k)$

$$\frac{1}{\varepsilon(k)} = 1 - \frac{4\pi n e^2}{k_B T k^2} S_{QQ}(k). \quad (3)$$

The above relation is valid only for an ionic system of undeformable ions obeying

TABLE (cont.)

Salt	$T_m^{a,b}$	Z_-	σ_+	σ_-	$C_{\alpha\beta}$	$H_{\alpha\beta}$	$P_{\alpha\beta}$	χ_M^d	$n^{a,b}$	Γ	S_{QQ}	
NiBr ₂ ^k	1236 (0.018)	0.53	0.78	1.85	0.0	1.51	0.0	1.09	0.0313	134	2.547	
					9.0	113	1.26					
					0.0	71.3	2.51					
NiCl ₂ ^k	1274 (0.016)	0.55	0.73	1.77	0.0	0.95	0.0	1.09	0.0369	138	2.720	
					5.8	98.1	1.04					
					0.0	54.4	2.09					
NiI ₂ ^k	1070 (0.031)	0.45	0.81	1.95	0.0	2.58	0.0	1.09	0.0250	142	2.495	
					19.0	182	1.48					
					0.0	122	2.95					
Salt	$T_m^{a,b}$	Z_-	σ_+	σ_-	$\rho_{\alpha\beta}$	$D_{\alpha\beta}$	$B_{\alpha\beta}$	χ_M^d	$n^{a,b}$	Γ	S_{QQ}	
CaBr ₂ ^l	1003 (0.05)	1.0	0.99	1.95		0.0	0.0	0.60	0.0279	156	2.815	
						2.95	265					
						3.03	0.015					
CaF ₂ ^m	1691 (0.05)	1.0	1.18	1.33	0.27		0.0	0.0	0.60	0.0575	116	2.898
							0.012					
							0.018					
CaI ₂ ^l	848 (0.05)	1.0	0.99	2.16		0.0	0.0	0.60	0.0219	170	2.934	
						2.59	215					
						3.03	0.015					
ZnBr ₂ ⁿ	667 (0.05)	1.0	0.74	1.95		0.0	0.0	1.44	0.0276	232	3.235	
						2.95	265					
						3.03	0.015					
ZnI ₂ ^l	719 (0.05)	1.0	0.74	2.16		0.0	0.0	1.44	0.0217	198	3.304	
						2.59	215					
						3.03	0.015					
MgBr ₂ ⁿ	984 (0.05)	1.0	0.65	1.95		0.0	0.0	1.28	0.0256	154	2.524	
						2.95	265					
						3.03	0.015					
MgI ₂ ^l	910 (0.05)	1.0	0.65	2.16		0.0	0.0	1.28	0.0196	152	2.731	
						2.59	215					
						3.03	0.015					
SrBr ₂ ^l	916 (0.05)	1.0	1.13	1.95		0.0	0.0	0.55	0.0268	168	2.850	
						2.95	265					
						3.03	0.015					
SrI ₂ ^l	788 (0.05)	1.0	1.13	2.16		0.0	0.0	0.55	0.0215	180	2.965	
						2.59	215					
						3.03	0.015					
BaBr ₂ ^l	1123 (0.05)	1.0	1.35	1.95		0.0	0.0	0.50	0.0240	132	3.108	
						2.95	265					
						3.03	0.015					
BaI ₂ ^l	1013 (0.05)	1.0	1.35	2.16		0.0	0.0	0.50	0.0193	136	3.137	
						2.59	215					
						3.03	0.015					
MgCl ₂ ^o	987 (0.024)							1.28			2.753	
CaCl ₂ ^o	1055 (0.061)							0.60			2.035	
BaCl ₂ ^o	1235 (0.066)							0.50			2.086	
SrCl ₂ ^o	1148 (0.06)							0.55			2.681	
ZnCl ₂ ^o	548 (0.028)							1.44			2.392	

TABLE (cont.)

Salt	$T_m^{a,b}$	Z_-	σ_+	σ_-	$C_{\alpha\beta}$	$H_{\alpha\beta}$	$P_{\alpha\beta}$	χ_M^d	$n^{a,b}$	Γ	S_{QQ}
YCl ₃ ^p	953 (0.05)	0.3	1.02	1.72	0.08	38.2	0.45	0.66	0.0307	252	1.326
					6.30	86.4	0.33				
					0.69	131	1.51				
YBr ₃ ^p	1177 (0.02)	0.3	0.90	1.96	0.08	9.64	0.45	0.66	0.0257	204	1.724
					9.96	213	0.43				
					0.88	192	1.96				
CeCl ₃ ^p	1095 (0.05)	0.3	1.01	1.81	0.0	34.3	0.0	0.7025	0.0316	222	1.478
					6.30	122	0.33				
					0.0	169	1.48				
CeI ₃ ^p	1025 (0.047)	0.3	1.01	2.20	0.0	34.3	0.0	0.7025	0.0212	207	1.702
					20.1	478	0.64				
					0.0	542	2.88				
LaCl ₃ ^p	1143 (0.05)	0.3	1.03	1.81	0.25	43.4	0.84	0.705	0.0312	210	1.422
					6.30	122	0.33				
					1.19	181	1.53				
ErCl ₃ ^p	1046 (0.035)	0.3	1.02	1.68	0.08	38.2	0.45	0.68	0.0316	237	1.691
					6.30	72.5	0.33				
					0.68	114	1.51				
ErBr ₃ ^p	1223 (0.024)	0.3	0.89	1.96	0.08	8.53	0.45	0.68	0.0250	189	1.717
					9.96	213	0.43				
					0.86	186	1.96				
ScCl ₃ ^p	1212 (0.034)	0.3	0.75	1.81	0.02	1.21	0.23	0.67	0.0262	192	1.742
					6.30	122	0.33				
					0.38	69.6	1.50				
HoCl ₃ ^p	993 (0.02)	0.3	1.01	1.70	0.0	35.0	0.0	0.6825	0.0324	255	1.670
					6.30	78.5	0.33				
					0.0	118	1.48				
HoBr ₃ ^p	1187 (0.03)	0.3	0.90	1.96	0.0	9.76	0.0	0.6825	0.0255	195	1.675
					9.96	213	0.43				
					0.0	192	1.93				
TbCl ₃ ^p	861 (0.03)	0.3	0.92	1.81	0.0	12.7	0.0	0.6875	0.0325	291	1.701
					6.30	122	0.33				
					0.0	127	1.48				
GdCl ₃	882 ^r (0.05)	0.3	0.94 ^c	1.81 ^c	0.0	15.2	0.0	0.69	0.0306 ^s	273	1.658
					6.30	122	0.33				
					0.0	134	1.48				
DyCl ₃	991 ^r (0.05)	0.3	0.91 ^c	1.71 ^c	0.0	11.2	0.0	0.685	0.0298 ^s	240	1.723
					6.30	82.1	0.33				
					0.0	87.9	1.48				
NdCl ₃	1057 ^r (0.05)	0.3	0.98 ^c	1.81 ^c	0.0	25.4	0.0	0.6975	0.0290 ^s	225	1.611
					6.30	122	0.33				
					0.0	155	1.48				
AlCl ₃	453 (0.03)	0.3	0.53 ^c	1.81 ^c	0.0	0.03	0.04	1.66	0.0234	495	1.958
					6.30	122	0.33				
					0.62	31.8	1.49				

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classical statistical mechanics. The Bhatia–Thornton charge–charge structure factor is defined as

$$S_{QQ}(k) = \sum_{\alpha} \sum_{\beta} Z_{\alpha} Z_{\beta} (c_{\alpha} c_{\beta})^{1/2} S_{\alpha\beta}(k), \quad (4)$$

where $Z_{\alpha,\beta}$, $c_{\alpha,\beta}$ and $S_{\alpha\beta}(k)$ are the effective charges, number concentrations and the partial structure factors, respectively. As usual, the $S_{\alpha\beta}$ is the Fourier transform of the pair radial distribution function of $g_{\alpha\beta}(r)$ which can be evaluated by using the liquid state theories in conjunction with the Ornstein–Zernike integral equation [16]. Numerous monovalent, divalent and trivalent halides are studied through the HNC approximation except for MgCl_2 , CaCl_2 , BaCl_2 , SrCl_2 , and ZnCl_2 for which $\varepsilon(k)$ is deduced from the experimental partial structure factors [17].

We shall concern two types of effective pair potential to model the interactions between the ion pairs: the Huggins–Mayer (HM) [18] form

$$\phi_{\alpha\beta}(r) = B_{\alpha\beta} \exp((\sigma_{\alpha} + \sigma_{\beta} - r)/\rho) + \frac{Z_{\alpha}Z_{\beta}}{r} - \frac{C_{\alpha\beta}}{r^6} - \frac{D_{\alpha\beta}}{r^8}, \quad (5)$$

which is used for the systems that have purely ionic character, and the Vashishta–Rahman (VR) [19] form

$$\phi_{\alpha\beta}(r) = \frac{H_{\alpha\beta}}{r\eta_{\alpha\beta}} + \frac{Z_{\alpha}Z_{\beta}}{r} - \frac{P_{\alpha\beta}}{r^4} - \frac{C_{\alpha\beta}}{r^6} \quad (6)$$

for the covalent systems, where $\eta_{\alpha\beta}$ and $P_{\alpha\beta}$ denote ionic radii. $Z_{\alpha,\beta}$ are the full charges for HM and effective charges for VR type of interactions. The terms and parameters have the usual meanings which are discussed in the corresponding references given in Table. In each row, the first line is for cation–cation, the second is for anion–anion and the third line is for the unlike ion pairs.

3. Results and discussion

Firstly, we pay attention to the amplitude of the correlation function between charge density fluctuations, $S_{QQ}(k_0)$. Numerical calculations are carried out with HNC approximation using the method due to Gillan [20] for $M = 2048$ mesh points at the temperature T . The calculation temperature is about five percent above the melting point except for the system that the number density is not available as a function of temperature (see the values in brackets in Table). The systems that we have studied cover, to a very large extent, all the systems in these families. The results for $S_{QQ}(k_0)$ are listed in the last column of Table. The values in brackets are taken from experimental data for a few systems for comparison. The agreements between the theoretical (or molecular dynamics simulation, see related references given in Table) and available experimental results in static structure justifies the use of functional form of the model potentials and parameters. We have found that $S_{QQ}(k_0)$ have the values approximately between 2.7–3.8 for monohalides, 2.0–3.2 for dihalides and 1.3–2.0 for trihalides. Extrapolation of the results for the systems that the density is available as a function of the temperature, the height of the main peak of the structure factors attain a value at the freezing temperature which is roughly 5% higher than the $S_{QQ}(k_0)$ listed in Table. This suggests that the $S_{QQ}(k_0)$ at freezing for monohalides is about 3.5. For comparison, it was estimated by MT that $S_{QQ}(k_0) \approx 5$ for alkali

halides. Freezing is realized into a crystalline phase with more strongly pronounced static correlations, which indicates the higher degree of short-range ordering, as the difference between the valence of metal and halogen ion decreases. It is also stated that a large value of the structure factor implies a small value for the free energy spent in modulating the homogeneous liquid density [8]. It seems that the simple rule, the structure factor has constant amplitude along the freezing line of alkali halides proposed by MT, cannot be implied to the whole halide salts as the predicted value of $S_{QQ}(k_0)$ varies between 1.3–3.8. However, the results suggest that $S_{QQ}(k_0)$ can be taken as constant for the group of systems which have the same stoichiometry. The average value of $S_{QQ}(k_0)$ is obtained as about 3.3 for monohalides, 2.8 for dihalides and 1.7 for trihalides. Considering the 1:1 case, it is known that for simple liquids, e.g. alkali halides the partial structure factors of anions and cations are almost identical by symmetry resulting with only weakly coupled density fluctuations and charge fluctuations, i.e. $S_{NQ}(k) \cong 0$. Whereas for the systems which freeze into a SIC phase where there is a significant electron density along a line between two atomic centers, namely bonding is directional, the fluctuations are more strongly coupled. There is a richer behavior in charge and density fluctuations when charge asymmetry is taken into account. The $S_{QQ}(k)$ has less prominent structural feature and $S_{NQ}(k)$ indicates more strongly coupled fluctuations as the difference between the number of anions and cations is increased.

In the second part of this paper we focus on the static dielectric function $\varepsilon(k)$ which can be obtained from $S_{QQ}(k)$ (see Eq. (2)). It is well known that the behavior of $\varepsilon(k)$ is connected with the freezing mechanism [15, 22]: the crystallization of a fluid is realized when $\varepsilon(k)$ is closest to k -axis in the negative region at the position k_0 where $S_{QQ}(k)$ has also its principal peak and which corresponds to the reciprocal lattice vector into which cooled liquid freezes. The results are presented in Fig. 1 where $\varepsilon(k_0)$ against k_0a are plotted, where $a = (3/4\pi n)^{1/3}$ is the mean ion sphere radius. The $\varepsilon(k_0)$ provides important insights of the freezing of salts. The instability in the liquid phase near freezing seems more desirable for monovalent halides compared to divalent and trivalent halides, as, in general, $\varepsilon(k_0)$ is closer to zero values in the negative region in the order of 1:1, 1:2 and 1:3. In addition, k_0a varies approximately between 2.5–4.5 ($k_0 \cong 1.4$ – 2.2 \AA^{-1}). This interval is occupied from left to right by 1:3, 1:1 and 1:2 but some of 1:2 systems are distributed towards the middle range of k_0a for the reasons we shall try to explain later. The solid line in Fig. 1 represents the sixth order polynomial fit of $\varepsilon(k_0)$ data. The behavior of this function resembles the behavior of the static dielectric function, $\varepsilon(k)$, of an ionic fluid which is also included as inset in Fig. 1. In the inset there is plotted $\varepsilon(k)$ versus ka for AgI, MgCl₂ and YCl₃ taken as representative samples. This reveals that the value of $\varepsilon(k_0)$ for each system lies about a curve which can be defined by a function that behaves like $\varepsilon(k)$.

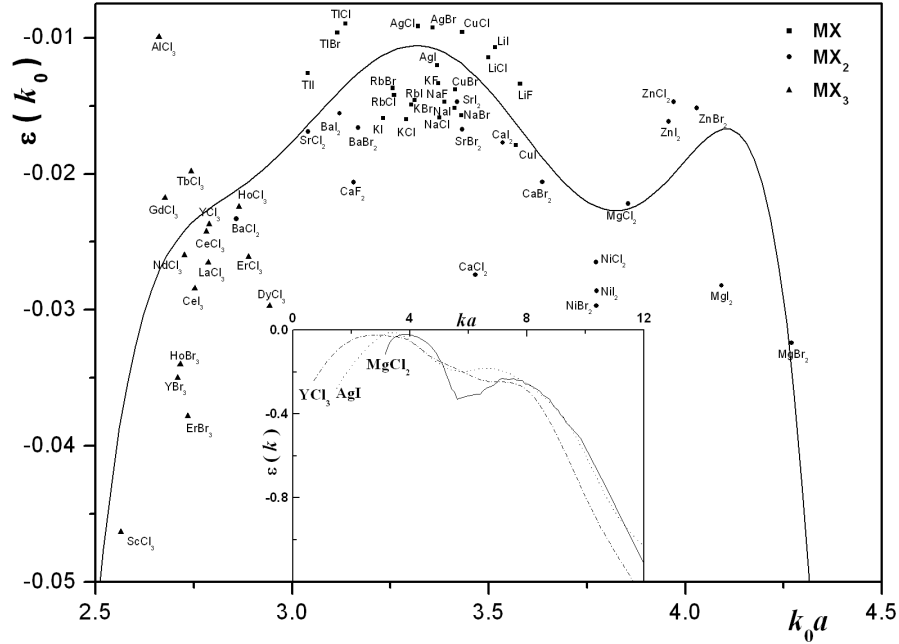


Fig. 1. The values of the first maximum of the static dielectric function $\varepsilon(k)$ plotted against k_0a , where k_0 and a are the positions of the first maximum of $\varepsilon(k)$ in reciprocal space and the mean ion sphere radius, respectively. The solid line represents the sixth order polynomial fit of $\varepsilon(k_0)$ data. The inset shows the $\varepsilon(k)$ versus ka for AgI, MgCl₂, and YCl₃ using different scale.

Chemical activity parameter χ_M proposed by Pettifor [21] for metal atoms (see Table) introduces a correlation with character of the chemical bonding, increasing χ_M corresponds to increasing weight of covalency against ionicity. This is clearly reflected in the behavior of $\varepsilon(k_0)$ by the tendency of a system, which has a higher activity parameter, generally, to take a place where $\varepsilon(k_0)$ is closer to zero. Silver, copper and thallium halides are well known to exhibit strong premelting phenomena and show similar structural behavior between their fast ion conducting crystalline phase and liquid phase, i.e. superionic phase can be described by a liquid-like picture. These systems generally occupy the top part of the first peak of $\varepsilon(k_0)$ which is closer to the zero signaling a more reinforced onset of freezing compared to simple salts i.e. alkali halides. Lithium halides are fairly typical ionic compounds. However, they have relatively low melting temperature, high chemical activity parameter and small cation size compared to other alkali halides. These differences are clearly reflected in the behavior of explaining the reason why LiX are found to behave differently from having similar behavior of the $\varepsilon(k_0)$ as seen in Fig. 1. Furthermore, strong similarities have been observed between the static structure of LiCl and CuCl melt [23, 24].

The first sharp diffraction peak (FSDP) is a characteristic feature of several MX_2 (M-metal ion and X-halogen ion) systems (molten and glassy systems, metallic alloys, molecular liquids, highly viscous network forming melts). FSDP gives information on the intermediate range order, in real space, occurring at low values of the scattering vector k , $k_{\text{FSDP}} \cong 1.0 \text{ \AA}^{-1}$. Many studies suggest that the FSDP is an evidence of directional bonding or high covalent character [17]. ZnCl_2 , NiI_2 , NiBr_2 , MgCl_2 , NiCl_2 , CaCl_2 , SrCl_2 and BaCl_2 , whose experimental structure factors are available, are ordered in terms of the FSDP from the most pronounced to the least. It is predominantly correct to say that if one of the halides has a FSDP the other two will also have. However, the height is more pronounced, in general, through the series Cl, Br, and I, for example nickel halides [17, 25–27]. The system with the low chemical activity parameter which usually means very small or non FSDP have the low covalency and migrates towards the middle where monovalent halides with the low χ_M are assembled. This behavior may look contrary to what has been observed in MX and MX_3 systems for which $\varepsilon(k_0)$ have closer value to zero as χ_M increased. However, the migration of the SIC divalent halides (e.g. SrCl_2 , CaF_2 , BaCl_2 , SrBr_2) towards the place where $\varepsilon(k_0)$ has its first peak also signals the onset of freezing as observed in 1:1 SIC even though different ions participate the freezing. According to the freezing theory into superionic phase [28], the freezing of SIC is driven by the marked ordering of the less mobile ion which is the anion for the monovalent SIC and the cation for the divalent SIC, whereas in the systems where the anion and cation have approximately equal mobility, for example alkali halides, both ions participate the freezing and the liquid phase is more stable compared to SIC at melt.

In spite of having the same type of crystal structure, the difference in melting mechanism between YCl_3 (and so DyCl_3 , HoCl_3 , and ErCl_3 due to similar liquid structure and melting mechanism) and AlCl_3 is reflected in the chemical scale, placing YCl_3 , ErCl_3 , HoCl_3 and DyCl_3 in a region of relatively high ionicity and AlCl_3 in a region of stronger covalency [29]. This feature in melting is also seen in freezing via that the $\varepsilon(k_0)$ of AlCl_3 , which has the higher χ_M , closer to ka -axis compared to the other MX_3 .

In a model of the Coulomb fluid, for example OCP, charge and density fluctuations can be calculated as a function of the plasma coupling parameter defined by $\Gamma = Z^2 e^2 / k_B T a$, where $Z^2 = \sum_i c_i Z_i^2$, c_i is the number concentration of ion i such that $\sum_i x_i = 1$. By analogy with the one-component plasma due to MT, the plasma parameter for halide salts are estimated at the temperature and densities used in this work and given in Table. The critical Γ of the molten alkali halides at freezing is clearly constant and has the value about one half of that for the classical OCP. These are consistent with the values estimated by MT for the alkali halides. However, for SIC or fast ion conductors in which one of the constituent ions is more mobile, usually the smaller one, the plasma parameter, generally, is about $\Gamma \cong 100$. As shown for copper halides the $\varepsilon(k)$ mimics the

behavior of $\varepsilon(k)$ of OCP at about $\Gamma \cong 90$ [31]. These higher critical values of the plasma parameter of fast ion conductors compared to that of ordinary solids just above the melting temperature, in our view, reflect the large differences in mobility of the cations and anions, which, coupled with their size differences, resemble a plasma of more mobile ions in the locally ordered background of the oppositely charged ions. Similar statements can be made for 1:2 and 1:3 salts and the Γ increases as the difference between the number of anions and cations is increased.

Finally, we take the issue with the supercooling estimation by Fasolino et al. [14] for NaCl, by the type of argument developed by Schneider et al. [30] for monatomic simple liquids, from $S_{QQ}(k_0, T_m)$ as $(T_m - T)/T_m \sim 1/S_{QQ}(k_0, T_m)$, if that is applied to the whole family of the systems studied here, it gives the results of $(T_m - T)/T_m \approx 0.31$ for monohalides which is in agreement with the estimation of Fasolino et al. [14], 0.36 and 0.63 for divalent and trivalent halides, respectively.

4. Conclusions

To conclude, we have analyzed the static freezing criteria and the freezing mechanism of halide salts from the height of the principal peak of charge-charge static structure factors and the static dielectric function. The charge-charge structure factor is found to be constant at freezing providing that whole family of the systems have the same effective charge difference. The freezing into crystalline phase is associated with the more strongly pronounced static correlations through the series of monovalent, divalent and trivalent halides. The critical value of the plasma parameter is affected by the difference in mobility and the number of constituent ions. The values of $\varepsilon(k_0)$ along the freezing seem to form a curve that can be represented by a sixth order polynomial which behaves like $\varepsilon(k)$ of a system near freezing. The distribution of the salts is determined by the stoichiometry and the ordering of ions and related to the onset of freezing, i.e. the system which freezes into superionic conducting crystalline phase shows the tendency to take the place where $\varepsilon(k_0)$ has its first peak which is closer to zero. Moreover, higher value of the chemical activity parameter or a pronounced first sharp diffraction peak corresponds to a higher value of $\varepsilon(k_0)$ in negative region reflecting the instability of the liquids with covalent nature. Further extensions of this work would be to study the dynamical freezing criterion for molten salts following the similar idea in the work by Pesché et al. [5, 6].

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