Charge-Charge Liquid Structure Factor and the Freezing of Alkali Halides

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Letter

Charge-Charge Liquid Structure Factor and the Freezing of Alkali Halides

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The peak height of the charge-charge liquid structure factor S_{QQ} in molten alkali halides is proposed as a criterion for freezing. Available data on molten alkali chlorides, when extrapolated to the freezing point suggests $S_{QQ}^{max} \sim 5$.

Following the very substantial progress made over the last decade in understanding second-order phase transitions, the problem of first-order transitions is of considerable current interest. Here, we are concerned with freezing, but specifically in systems where Coulomb interactions are a dominant feature.

In a two-component liquid, such as an alkali halide, it is structurally necessary to use three partial structure factors. For our present purpose, the number-charge structure factors are the appropriate tools. It is known that in molten NaCl[1,2] the number-number structure factor $S_{NN}(k)$ is rather gas-like, while the cross-correlation function $S_{NQ}(k)$ has very little structure. The charge-charge correlation function $S_{QQ}(k)$, in contrast, shows a very prominent principal peak and qualitatively resembles the structure factor of an ordinary monatomic liquid just above the freezing point.

Now we can enquire what are the structural analogues of S_{QQ}, etc., in the ideal crystalline state. In a monatomic crystal, this would lead us to the order parameters as the Fourier components ρ_G of the periodic atomic density, G being the reciprocal lattice vectors. This has as an obvious generalization in an ionic crystal the Fourier components of $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$, the

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periodic densities of cations and anions respectively. The number and charge densities $\rho_+ + \rho_- \equiv \rho_N$ and $\rho_+ - \rho_- \equiv \rho_Q$ may evidently be Fourier decomposed and yield the full set of order parameters for the ionic crystal.

In the NaCl rockstalt structure, for instance, ρ_N is describing the simple cubic lattice which is the structure if the differences between cations and anions are ignored. ρ_Q on the other hand is crucially describing the differences between anions and cations and thus is characterizing the ionic crystal as a face-centered-cubic lattice with a basis. Since ρ_Q is therefore reflecting directly the ionic character, and more specifically the alternation of the ionic charges in the crystal structure, it contains the basic fact that the cohesive forces are Coulomb in nature.

The link between ρ_N and ρ_Q in the crystal and the liquid structure factors is that we must correlate the fluctuations $\rho_N(\mathbf{k})$ and $\rho_Q(\mathbf{k})$ in the liquid to generate $S_{QQ}(k)$, etc., as $\langle \rho_Q(\mathbf{k})\rho_Q(-\mathbf{k})\rangle$, $\langle \rho_N(\mathbf{k})\rho_N(-\mathbf{k})\rangle$ and $\langle \rho_N(\mathbf{k})\rho_Q(-\mathbf{k})\rangle$. In view of the discussion of the role of ρ_Q in the crystal, it is not surprising, as the experimental evidence quoted above for molten NaCl indicates, that the residual short-range ordering in the ionic liquid is reflected primarily in $S_{QQ}(k)$. This is therefore the basic quantity we shall focus on below in proposing a criterion for freezing: more particularly we shall direct attention to its principal peak height S_{QQ}^{max}.

To motivate the criterion, we note first that in one model Coulomb fluid, the classical one-component plasma, $S_{QQ}(k)$ can be calculated essentially exactly by computer simulation[3,4] as a function of the plasma coupling parameter Γ defined by

$$\Gamma = e^2/(k_B T a) \tag{1}$$

where a is the mean interparticle spacing defined in terms of the number density n by

$$n = 3/(4\pi a^3). \tag{2}$$

The freezing transition, to a body-centred cubic lattice, occurs at a critical value $\Gamma \simeq 160$. Corresponding to this critical value of Γ, the value of S_{QQ}^{max} is found to be 2.7. It should be mentioned here that this classical one-component plasma has already offered a basis for calculating pure liquid metal structure factors[5] and for a criterion for freezing of alkali metals.[6] Related considerations on neutral monatomic systems are in the work of Hansen and Verlet[7] and of Ramakrishnan and Yussouff.[8]

Returning now to the molten alkali halides, we argue that a similar criterion for freezing should involve primarily S_{QQ}^{max}. Two essential differences immediately arise in discussing S_{QQ}^{max} for the molten alkali halides. Obviously, we are dealing with a two-component plasma, and equally important, we have ionic radii playing an essential role. We believe that the main features

of the freezing of alkali halides would appear in a model of a mixture of charged hard spheres, if it could be solved by computer simulation. In addition to the plasma parameter Γ in (1), the ionic radii R_+ and R_- would clearly enter the structure factors. In the absence of such a detailed study, we shall immediately appeal to neutron diffraction experiments on the molten alkali chlorides.

The values of S_{QQ}^{max}, all at temperatures slightly above the melting point, are recorded in the Table.

<div align="center">TABLE I</div>

<div align="center">Height of principal peak in S_{QQ}</div>

	NaCl[1]	KCl[9]	RbCl[10]	CsCl[9]
S_{QQ}^{max}	3.2	4.4	3.6	3.1
$(T - T_m)/(T_m$	0.070	0.023	0.035	0.059
Γ	71	65	66	65

We have read the values of the partial structure factors required to calculate S_{QQ}^{max} off graphs of the published data and therefore S_{QQ}^{max} could be in error by a few units in the decimal place. Also recorded is the % deviation of the temperature of the measurements from the melting temperature T_M. If we extrapolate back to the melting temperature, we find a value of $S_{QQ}^{max} \sim 5$. Of course there is a variation of radius ratio through the Table and presently we have no means of telling how this will affect S_{QQ}^{max}. We think, however, that it is of interest to have experiments from which the peak height S_{QQ}^{max} can be obtained as near to the freezing point as is feasible.

By analogy with the one-component plasma, we next use empirical data to estimate the plasma parameter Γ defined in Eq. (1) at the melting temperatures for the liquids in the Table. In making these estimates of Γ we have used the molecular volume in the crystal to calculate the density n. Since CsCl in the liquid is known to have coordination numbers close to six,[9] we have used the NaCl structure formula to calculate its molecular volume from the observed nearest neighbour distance in the crystal. As seen from the final row in the Table, the plasma parameter Γ is indeed remarkably constant at the melting point. Clearly, the critical Γ for freezing of the molten alkali halides is about $\frac{1}{2}$ of that for the one-component plasma. It seems to us that this reduction is largely due to finite ionic radii, but it would be of considerable interest if this point could be tested by computer simulation on a model of a mixture of charged hard spheres.

This constancy of Γ at freezing, and our interpretation of it in terms of the charge-charge structure factor, affords a ready explanation of the

results of Reiss *et al.*[11] who noted that the melting temperature of alkali halide crystals is directly correlated with $e^2/(R_+ + R_-)$, i.e. the sum of ionic radii. This differs from the constancy of Γ only by the replacement of a by $R_+ + R_-$. But the first neighbour interionic distances in the alkali halides are well known to obey an additivity law in terms of ionic radii, so that the criterion of Reiss *et al.*[11] and our own differ only by a scaling factor.

In summary, by focussing on the charge-charge structure factor, and by using the analogy with the classical one-component plasma, we have proposed a criterion for freezing in the alkali halides, namely that freezing will occur when the value of S_{QQ}^{max} reaches a value of about 5. This value is considerably larger than that in the one-component plasma, whereas the critical value of Γ for freezing of the alkali halides is considerably smaller. Of course, it remains an interesting question as to the way in which such criteria of freezing of the liquid relate to criteria for the melting of the crystal, such as Lindemann's law.

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