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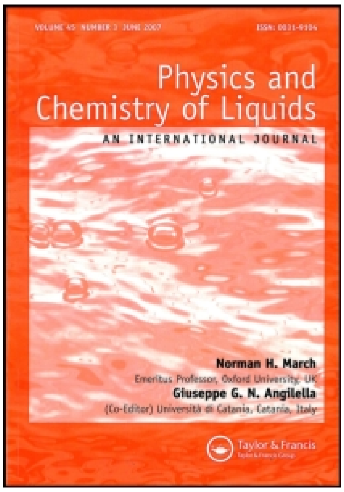

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Electronic and Ionic Ordering in Condensed Matter Plasmas. (Phase Transitions Induced by Coulomb Interactions)

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Review Article
Electronic and Ionic Ordering in Condensed Matter Plasmas†
(Phase Transitions Induced by Coulomb Interactions)

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Recent progress in treating phase transitions induced by Coulomb interactions is reviewed. This is done by appealing to simple models, and in particular to the one-component plasma, with its quantum-mechanical counterpart jellium. The relevance of the phase transition, to a body-centred-cubic crystal in the classical one-component plasma, to the freezing of liquid metals Na and K is stressed. By generalizing these arguments to a two-component system, regularities in the freezing of the molten alkali halides are understandable. Sublattice disorder in superionics, driven by Coulomb forces, is then discussed. Finally, the ordering of electrons in jellium, in the limit of complete degeneracy, is considered; evidence being presented for the existence of electron liquids in molten Na and K.

1 INTRODUCTION

While very considerable progress has been made in the theory of second-order transitions over the last decade or so, first-order transitions such as freezing of a liquid metal, or a molten salt, are much less well understood. However, while the problem of freezing remains difficult for the types of force law appropriate say in liquid argon, unless one resorts to computer experiment, there is a class of transitions induced by long-range Coulomb interaction in which our understanding of the way a phase transition can arise is much clearer. Even here, however, with the simplest possible classical model, the one-component plasma, to obtain firm quantitative results one must appeal to computer calculations but nevertheless one has a clear picture of what is happening as the phase transition occurs.

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† The content of this review is, in essence, that of an invited paper given at the York Conference of the Institute of Physics in January, 1981.

Furthermore, while initially the problem of phase transitions focused on the thermodynamic aspects, it has become fruitful more recently to move attention to the structure of the liquid phase. Thus, as the title of this review emphasizes, we shall be discussing phase transitions induced by Coulomb interactions in terms of ordering in the condensed matter plasmas. The idea of long-range order in the crystalline solid state needs little emphasis; one can, for instance, conveniently define the Fourier components of the periodic ion density as a set of order parameters to use in discussing the phase transition.

When we turn to the liquid phase, the appropriate tool to discuss the short-range order is known to be the radial distribution function $g(r)$, or its Fourier transform $S(q)$. This latter quantity is accessible experimentally, and if we consider its determination by X-ray scattering, then if $I(q)$ is the intensity of X-rays of incident wavelength λ scattered through an angle θ,

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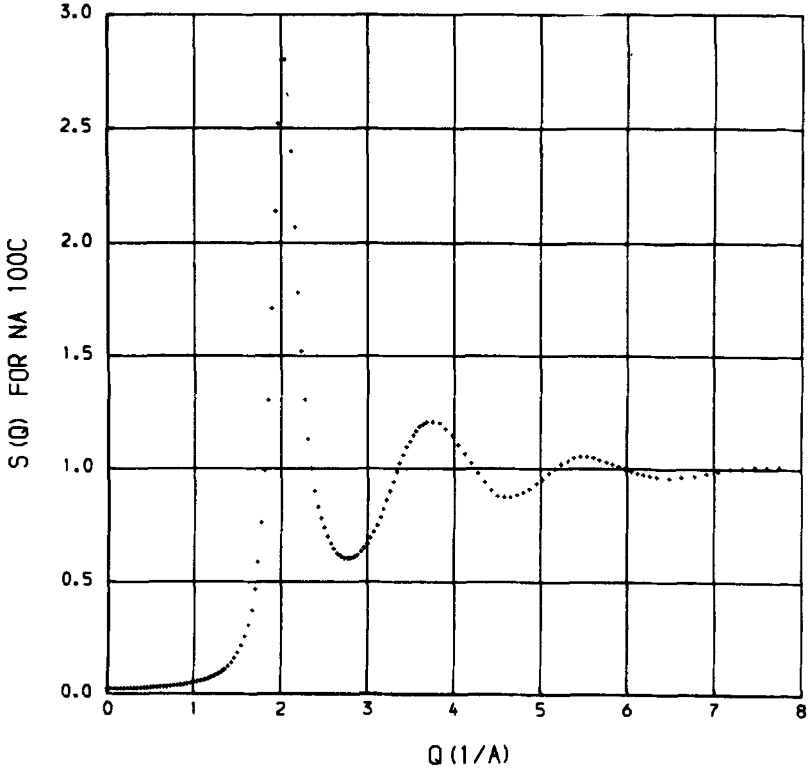

FIGURE 1 Structure factor of liquid Na at 100°C, obtained by X-ray scattering. After Greenfield *et al.* (Ref 1).

with $q = 4\pi \sin \theta/\lambda$, from a liquid sample of N atoms, one can write

$$I(q) = \mathrm{N}|f(q)|^2 S(q) \tag{1.1}$$

where $f(q)$ is the atomic scattering factor. The structure factor for liquid Na near its freezing point determined in this way by Greenfield *et al.*[1] is shown in Figure 1; we shall return to consider the height of its first peak around 2 Å^{-1} below. That systematics involving the first peak in the structure factor occur on freezing Lennard-Jones like liquids was known to Verlet,[2] and with such liquids in mind Ramakrishnan and Yussouff[3] have developed a theory of freezing. As already stressed, we are interested here in the consequences of the long-range Coulomb interaction in causing freezing. Though we shall approach this via models, we shall deal with (a) liquid metals, especially those with weak electron-ion interaction like Na and K, which have recently been focused on by Ferraz and the writer[4] and (b) ionic condensed phases. Specifically under (b), March and Tosi[5] have discussed the structure of molten salts near their freezing points, with reference to the alkali halides. Also under (b), brief reference will be made to the fluorite fast ion conductors, this area having recently been considered in more detail.[6]

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In the following section we shall begin the discussion of models in which the effects of Coulomb interactions are directly exposed. In this review we shall consider:

i) The one-component plasma. Here point particles carrying charges e move in a neutralizing uniform background which cannot respond. The important length in the problem is the mean interparticle spacing r_s. One has two important cases of (i); (a) the classical plasma, which we shall argue has relevance to the positive ions in Na metal, for which the conduction electrons are almost uniform because of the weak electron-ion interaction, and (b) the quantal plasma, or jellium, where interacting electrons which are completely degenerate move in a uniform positive background.

ii) Charged hard spheres, or a two-component plasma. This is relevant to molten alkali halides.

2 STRUCTURE AND PHASE TRANSITION IN A ONE-COMPONENT CLASSICAL PLASMA

From the length r_s introduced above, a measure of the Coulomb interaction energy is evidently e^2/r_s. The reason why the one-component plasma model is so attractive as a model system is that its properties are characterized by only one parameter Γ, which is defined as the ratio: Coulomb energy e^2/r_s to

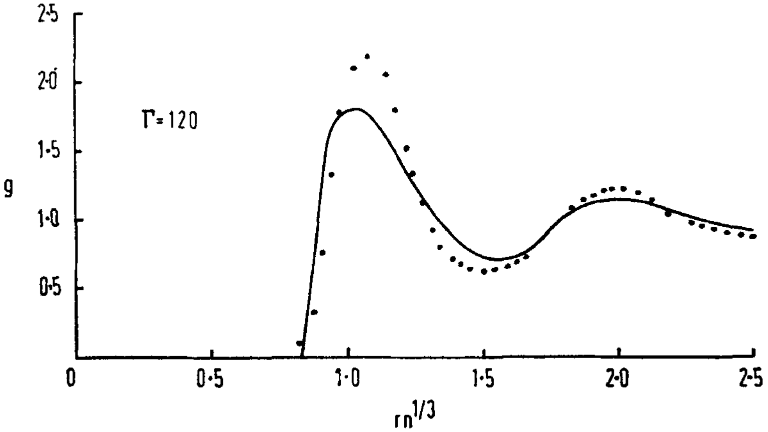

FIGURE 2 Pair distribution function $g(r)$ for classical one-component plasma. Dotted curve. Computer simulation (Ref. 8). Solid curve. Approximate analytic model (Ref. 7). Scale of length $rn^{1/3}$ is proportional to r/r_s.

thermal energy $k_B T$:

$$\Gamma = \frac{e^2/r_s}{k_B T}. \tag{2.1}$$

This means that the structure factor $S(q)$, or its Fourier transform $g(r)$, depend only on specifying the value of Γ in Eq. (2.1). Though approximate analytic theories[7] exist to allow $g(r)$ to be calculated in the liquid regime, these are not yet capable of predicting the phase transition to a crystalline state. Fortunately, the early computer experiments of Teller and his colleagues,[8] followed by the work of Hansen[9] and others, have made available precise quantitative results for (a) the radial distribution function $g(r)$ for a variety of values of the coupling parameter Γ in the fluid phase and (b) the critical value of Γ at which the one-component plasma freezes.

As regards (b), it was shown in Ref. 8 that the one-component classical plasma crystallizes when Γ exceeds a critical value of 160. For a smaller value of Γ, namely 120, Figure 2 shows the computer results (dotted curve) while in the solid curve the approximate analytic result of Gillan[10] is displayed. The short-range order in the ion liquid is clear and this short-range order will evidently become more pronounced as the critical Γ is approached. To make this point more explicit, Ferraz and March[11] have plotted the height of the first peak in $S(q)$ for the one-component plasma from the computer experiments and the curve shown in Figure 3 is then obtained. It will be seen that as Γ is increased from small values, i.e. from the Debye–Hückel regime, $S_{\max}$ increases from its "gas" value of unity to a value of 2.71

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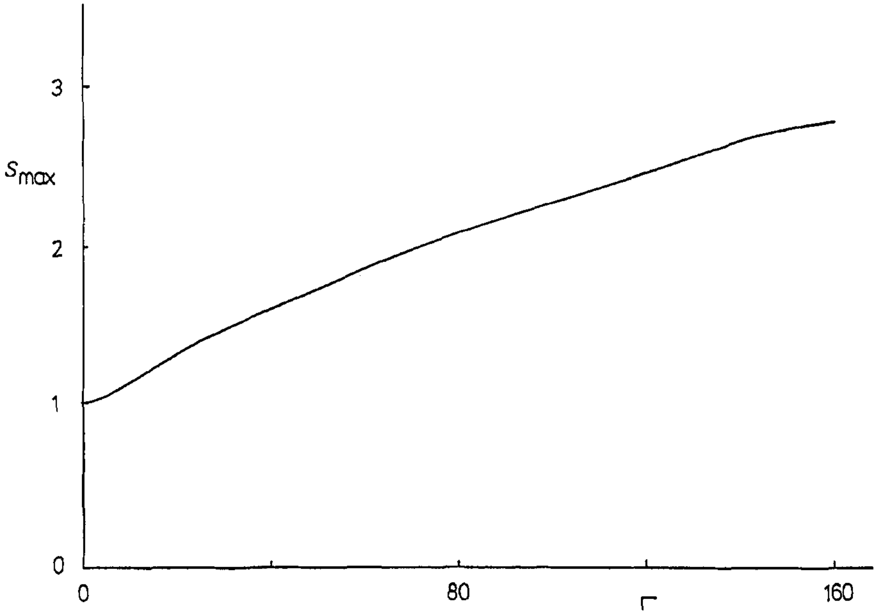

FIGURE 3 S_{max} versus coupling parameter Γ for one-component plasma (after Ferraz and March).[4]

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at the critical Γ of 160. Thus, alternative criteria for freezing of the one-component plasma are:

(I) The plasma freezes when the ratio: Coulomb energy divided by thermal energy is 160 or greater.

(II) The one-component classical plasma freezes when the principal peak of its structure factor reaches a height $S_{max} = 2.71$.

3 FREEZING OF LIQUID ALKALIS Na AND K

This is the point at which we want to confront the criteria (I) and (II) above for freezing of the classical one-component plasma with experimental facts on the liquid alkali metals Na and K. The reasons why it is tempting to regard these two liquid metals as ideal candidates for a description by such a model are (a) their small ion cores and (b) their weak electron-ion interactions. Of course, for some purposes, and in particular for calculating the velocity of sound, it is essential to allow for the weak electron-ion interaction, thereby screening the ionic plasma frequency to yield an acoustic phonon dispersion relation at small k. Ivanov *et al.*[12] pointed out the numerical relevance of criterion (I) to the melting curve of Na, and very recently Ferraz and March[11] have drawn attention to the fact that liquid Na and liquid K freeze when the height $S_{\max}$ of the structure factor becomes respectively 2.80 (at 373 K; cf. Figure 1 for result of Greenfield *et al.*) and 2.73 (338 K).

The second point to be made here is that the freezing of the one-component plasma takes place to a body-centred-cubic structure. This is also very attractive in that liquid Na and K freeze into this crystalline phase. For the model, Wigner[13] had earlier anticipated that the completely degenerate limit would freeze into a body-centred cubic structure in order to lower the Madelung energy of a lattice of point charges in a uniform background below that of other structures.[14] Therefore, the one-component plasma transition can be referred to as "classical Wigner crystallization."

Of course, it can be argued, as mentioned above in the discussion of acoustic phonons in Na and K, that the long-range Coulomb interactions are screened. Nevertheless, the recent work of Ross[15] has compared thermodynamic calculations on the molten alkalis using different reference liquids, e.g. hard sphere and one-component plasma, and he has concluded that the one-component plasma is the best reference liquid available to us presently for discussing liquid Na. Of course, electron-ion interaction then has to be introduced in the well-known manner via pseudopotential theory. To get Lindemann's Law of Melting, such pseudopotential corrections are quite essential. But as Tosi and his colleagues have shown,[16] the full structure factors of the simple liquid alkalis can be very usefully approximated by starting from the one-component plasma structure.

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4 CHARGE-CHARGE LIQUID STRUCTURE FACTOR $S_{QQ}(q)$ AND FREEZING OF ALKALI HALIDES

Having established the interest in the principal peak of the structure factor $S(q)$ for one-component systems, we turn to effect a generalization to the two-component charged fluids, of which the simplest are the molten alkali halides. The discussion below is based on the work of March and Tosi.[5]

In connection with the one-component systems discussed so far, we referred to the crystalline state as being characterized by order parameters which were the Fourier components of the periodic ionic density. The generalization to an ionic crystal like NaCl is clear. One introduces the Fourier components of the periodic densities of cations and anions, $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$. We then define the number density $\rho_N = \rho_+ + \rho_-$ and the charge density $\rho_Q = \rho_+ - \rho_-$, and Fourier decompose these. Then, in place of the three partial radial distribution functions $g_{\mathrm{Na-Na}}$, $g_{\mathrm{Cl-Cl}}$ and the crosscorrelation $g_{\mathrm{Na-Cl}}$, or the corresponding partial structure factors, it is helpful for our present purposes to work with the number-charge structure factors defined by

$$\left.\begin{aligned} S_{NN}(q) &= \langle \rho_N(q)\rho_N(-q)\rangle \\ S_{NQ}(q) &= \langle \rho_N(q)\rho_Q(-q)\rangle \\ S_{QQ}(q) &= \langle \rho_Q(q)\rho_{-Q}(-q)\rangle \end{aligned}\right\} \tag{4.1}$$

If one examines neutron experiments on molten NaCl, one finds that if one forms the above structure factors from the data then (i) $S_{NN}(q)$ is rather gas-like, (ii) $S_{NQ}(q)$ exhibits very little structure and (iii) $S_{QQ}(q)$ has a prominent principal peak and qualitatively resembles $S(q)$ of an ordinary one-component liquid just above its freezing point.

Therefore, March and Tosi[5] have studied the available experimental data on the molten alkali halides for the height of the principal peak in S_{QQ} and Table I is taken from their work.

TABLE I

Experimental results for height of principal peak of charge charge structure factor S_{QQ} in molten alkali halides

	NaCl[17]	KCl[18]	RbCl[19]	CsCl[20]
$S_{QQ}^{\max}$	3.2	4.4	3.6	3.1
$(T - T_m)/T_m$[a]	0.070	0.023	0.035	0.059
Coupling parameter	71	65	66	65

[a] T_m is the observed melting temperature. T is the temperature of the neutron measurements of structure factors. The coupling parameter for this "two-component plasma" is defined in analogy with Eq. (2.1), r_s being the mean interparticle spacing.

It is gratifying, following the previous discussion on the one-component plasma, that at freezing the coupling parameter is nearly constant, and as defined is around 67 ± 3. This corresponds, of course, to criterion (I) above for the one-component plasma. As regards criterion (II), it will be seen from the second row of Table I that the measurements recorded are at different temperatures relative to the melting point. March and Tosi[5] have made an extrapolation, which is long and therefore somewhat rough, of this data to T_M and they estimate

$$S_{QQ}^{\max} \sim 5 \tag{4.2}$$

at melting. It has to be cautioned however that there is a variation of radius ratio through Table I, and though it is not large we have presently no means

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of telling how this will affect $S_{QQ}^{\max}$. But that care is needed with a wide variation is clear from the results of Gillan *et al.*[21] that for large radius ratio and strong coupling a two-component plasma will eventually polymerize and there will then be a coordination number of two. It seems clear that the type of criteria presented in this article will be reliable when there is little change in coordination number on melting.

It is of interest here also[5] to comment that Reiss *et al.*[22] have pointed out that the melting temperature of ionic crystals is directly correlated with $e^2/(R_+ + R_-)$, that is with the inverse of the sum of ionic radii. The constancy of the coupling parameter in Table I, anticipated from the plasma models underlying the present discussion, affords a ready explanation. For this criterion of constant Γ gives the melting temperature as being inversely proportional to the near-neighbour distance a. But first neighbour interionic distances in alkali halides are well known to obey an additivity law in terms of ionic radii and thus the connection of the plasma criterion with the work of Reiss *et al.*[22] can be established.

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5 DEBYE-HÜCKEL MODEL OF SUPERIONICS

In this review of phase transitions induced by Coulomb interactions, we wish at this point to refer to fast ion conduction in the fluorite structure. We can be quite brief here, as a recent review of this area is already available.[23]

The important point here is to establish whether, in the transition to a state of fast ion conduction, the Coulomb interaction between charged Frenkel defects can induce the superionic transition. This has been considered recently by March *et al.*[24] Their work follows Lidiard[25] including the interaction between charged defects by Debye-Hückel theory, which we referred to briefly in Section 2 above. Such an approach was used to treat melting of ionic crystals in terms of Schottky defects by Kurosawa:[26] but March *et al.*[24] emphasize that the Kurosawa type transition, modified to apply to Frenkel defects, may well be much more appropriate to explain the transition to the superionic state than to treat melting, for which the plasma picture of the previous section seems to afford a more fundamental approach.

The idea is simply stated; it is to treat charged anion vacancies and anion interstitials by electrolyte theory, as moving in a medium with dielectric constant ε. Though the (fluorite) lattice is not incorporated explicitly in the model, one introduces a length a as the distance of closest approach of a vacancy and an interstitial.

Linear Debye–Hückel theory[27] then leads to the chemical potential μ of either vacancy or interstitial as

$$\mu = -\frac{e^2K}{2\varepsilon(1 + Ka)} \tag{5.1}$$

where K^{-1} is the Debye–Hückel shielding length given by

$$K^2 = \frac{8\pi\rho e^2}{\varepsilon k_B T} \tag{5.2}$$

ρ being the density of Frenkel defects.

5.1 Instability induced by Coulomb interaction between Frenkel defects

In connection with the thesis of this review, we want to stress here that the Coulomb interaction leads to an instability of the assembly of interacting Frenkel defects above a certain temperature T_c. Thus, if we write the concentration c of Frenkel defects in terms of its Arrhenius value c_0 for non-interacting defects and the chemical potential μ in Eq. (5.1) we obtain

$$c = c_0 \exp\left(-\frac{\mu}{k_B T}\right). \tag{5.3}$$

The chemical potential is evidently dependent on c and from Eq. (5.1) is leading to an enhancement of the Frenkel defect concentration over its Arrhenius value c_0. As the temperature is raised, there is a cooperative manifestation of the interactions in reducing the Frenkel formation energy which leads to no solution of Eq. (5.3) for c above a temperature T_c. This instability occurs at concentration c_c given by

$$c_c = f\left(\frac{k_B T_c}{(e^2/\varepsilon a)}\right), \tag{5.4}$$

where the form of the function f is determined by the Debye–Hückel theory.

5.2 Relation to disordering transition to fast ion conduction in fluorites

In relation to our discussion of the transitions induced in one and two component plasmas, at a critical value of the coupling parameter Γ of Eq. (2.1), it is of interest that the critical concentration c_c is determined by the ratio of Coulomb energy $e^2/\varepsilon a$ to $k_B T_c$. If we use experimental data, it turns out that for CaF_2, SrF_2 and BaF_2, this ratio at the superionic transition is, within experimental error, the same for these three fluorites. Thus, for these three materials, the transition will occur according to Debye–Hückel theory at the same critical concentration c_c.

Solving the Debye–Hückel equations for the temperature of the instability, which is identified with the superionic transition to a disordered sublattice

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configuration, the temperature is found to be given by[27] ($K_c = K(T_c)$)

$$k_B T_c = \frac{e^2 K_c a}{4\varepsilon a(1 + K_c a)^2}. \tag{5.5}$$

This formula is sensitive to the choice of distance of closest approach a. If one chooses a to get the correct T_c for CaF_2 as an example, one finds[27] $c_c \sim 3\%$ and a to be about $\frac{1}{2}$ of the F–F distance which does not seem unreasonable. It is tempting to think of the disorder above T_c in terms of sublattice melting, but Catlow has argued strongly against such a picture.[28]

6 ELECTRON LIQUIDS AND ELECTRON CRYSTALS

The discussion so far has centred round assemblies which are classical. We want to conclude this review by discussing completely degenerate electron assemblies and asking whether electronic order can exist due to Coulomb repulsions between the electrons. A major advance in such a discussion was due to Wigner,[29] who considered electronic order in the jellium model of a simple metal. As remarked above, jellium is a quantum system of interacting electrons moving in a uniform positive neutralizing background which is not allowed to respond.

As remarked previously, the essential parameter is the mean interelectronic distance r_s. Wigner pointed out that in the low density limit when r_s exceeded a certain critical value, the electrons would crystallize on to a body-centred-cubic lattice to lower the Madelung energy. We still do not know the critical value of r_s with the same certainty that we know the critical Γ in the classical one-component plasma, because clearly the quantum-mechanical Wigner crystallization is a more profound matter than its classical analogue. However, the lowest electron density metal, Cs, has an r_s of 5 Bohr radii, and clearly the electrons are delocalized since it is metallic. As reviewed by Care and March,[30] many theoretical estimates of the critical r_s exist, ranging from 10 to 300 Bohr radii, but current trends are towards a value of 60–80 Bohr radii. (See Note added in proof, p. 113.)

The electronic ordering as the transition is approached can be estimated and the pair functions $g(r)$ are shown in Figure 4. Curve (i) for $r_s \sim 100$ Bohr radii is estimated from the localized Wigner oscillator orbitals.[31] We see that the Fermi hole limit, r_s tends to zero, gives way to a regime of short-range order which we term an electron liquid, and this, as r_s increases, eventually gives way to a long-range ordered electron crystal.

The momentum distribution associated with the different regimes goes from the non-interacting Fermi distribution to a gaussian form for the electron crystal. It has been argued that in the metallic phase, at absolute

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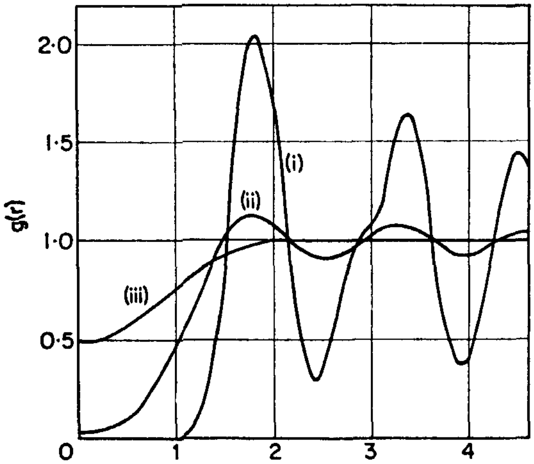

FIGURE 4 Pair distribution function for completely degenerate electrons in uniform background of positive charge, as mean density is varied. Lengths are measured in units of r_s. Curve (i) Low density. Electron crystallization has occurred. Curve (ii) Intermediate density. This is the regime of the electron liquid. Curve (iii) Electron gas. Fermi hole is drawn and is due entirely to statistical correlations.

zero, the discontinuity in the Fermi distribution is a useful order parameter to discuss the metal—localized electron crystal transition.[32]

6.1 Electron liquids in molten metals

Though a good deal of attention has focused on the possibility of electron crystals existing in (a) highly compensated semiconductors and (b) in two-dimensional situations, for example electrons on the surface of liquid helium,[30] we shall conclude this review by summarizing evidence in favour of the existence of an electron liquid in molten metals. That such a situation indeed obtains was first noted by Egelstaff *et al.*[33] They compared the structure factors for liquid metals with those of other liquids, the comparison being made by using neutron and X-ray data. In Table II, the intensity ratios they gave are summarized.

TABLE II

Group	$\frac{\text{Neutron peak height}}{\text{X-ray peak height}}$
Liquefied rare gases	0.98 ± 0.03
Molecular fluids	1.12 ± 0.04
Monovalent metals	0.87 ± 0.04
Polyvalent metals	0.92 ± 0.03

Attention is focused in this table exclusively on the height of the main peak. From the table, Egelstaff *et al.* concluded that since atomic form factors $f(q)$ in Eq. (1.1) had been used in obtaining the X-ray peak height, the first entry told us that the electrons, in say liquid argon, were distributed just as in a free space argon atom, while the second entry told us that chemical bonding had spread out the electrons in **r** space and made the scattering factor more compact in **q** space. This would bring X-ray and neutron results together in the molecular fluids considered. But similar delocalization of the valence electrons in the metals would, as Egelstaff *et al.* pointed out, enhance the "disagreement" between X-ray and neutron data. They concluded that there was longer-range order among the electrons than in the ions of molten metals.

Further work has been of three kinds: (i) experiments to get electron diffraction data[34] of comparable accuracy to available X-ray and neutron data, to enable the extraction of the pair correlation function[33] (cf. Figure 4) between conduction electrons, (ii) theoretical work to estimate the effect of weak-electron ion interaction on the electron pair correlation function[35] and (iii) an extension of the analysis of Egelstaff *et al.* away from the first peak, from available X-ray and neutron data.[36,37]

We restrict ourselves here to saying that Dobson[36] for Na, and Johnson[37] for K, have argued, following Egelstaff *et al.*,[33] that there is indeed electronic ordering. This, they propose, is usefully talked about in terms of reflections which are consistent with (local) face-centred-cubic ordering in liquid Na and K. March and Tosi[38] have made the suggestion that one can understand this in terms of a combination of electron-ion and electron-electron interactions, but since it has not yet proved possible to test their proposal experimentally we shall not go into it here.

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7 SUMMARY

Features associated with the Coulomb force have been emphasized in connection with phase transitions that it can induce. The argument has been built round plasma models. For the one-component classical plasma, two important results are well established:

a) The maximum value of the liquid structure factor, $S_{\max} = 2.71$. It has been argued that this is already relevant to the freezing of Na ($S_{\max} = 2.80$ at 373 K) and $K(S_{\max} = 2.73$ at 338 K).

b) $(e^2/r_s)/(k_B T_m) = 160$, r_s being the mean interparticle spacing and T_m the melting temperature.

Building on the above, molten salt data lead to the prediction that freezing should occur when:

c) the maximum value of the charge-charge structure factor is about 5, and

d) the coupling parameter corresponding to (b) above is near 70.

It would clearly be of interest if neutron measurements very near the freezing point could be made on a number of molten alkali halides to test the above, and in particular to see if there is significant dependence on radius ratio. Evidently, computer experiments on a mixture of positively and negatively charged hard spheres, with a radius ratio near to unity, would be worthwhile to complement existing results for large radius ratio.[21]

Though we have discussed superionics only rather briefly, it has been demonstrated that Coulomb interactions between Frenkel defects can drive the transition, and more work is to be expected from this standpoint.

Finally, after a brief survey of the theory of jellium, the results of diffraction experiments have been used to demonstrate that there is growing evidence for electron liquids, with quite a degree of short-range order, in molten metals.

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Acknowledgments

It is a pleasure to thank Professor M. P. Tosi for many valuable discussions on the area of this review, and for making available the work of his group on liquid metal structure factors, prior to publication. Many fruitful conversations with Dr M. J. Gillan are also acknowledged. My former colleagues at Imperial College, A. S. Brah, P. J. Dobson, and L. Virdhee, have kept me in touch with the diffraction programme on liquid metals and I am very grateful to them, and also to Dr M. Johnson for showing me his neutron data on liquid K, prior to publication.

Note added in proof.

The Monte Carlo study of Ceperley and Alder (*J. Phys. Colloq* (*France*), **41**, No. C-7, p. 295–8, 1980), has confirmed that the Wigner transition in jellium occurs at r_s around 100 Bohr radii.

References

1. A. J. Greenfield, J. Wellendorf, and N. Wiser, *Phys. Rev.*, **A4**, 1607 (1971).
2. L. Verlet, *Phys. Rev.*, **184**, 150 (1969).
3. T. V. Ramakrishnan and M. Yussouff, *Solid State Commun.*, **21**, 389 (1977).
4. A. Ferraz and N. H. March, *Solid State Commun.*, **36**, 977 (1980).
5. N. H. March and M. P. Tosi, *Phys. Chem. Liquids*, **10**, 185 (1980).
6. N. H. March, *Phys. Chem. Liquids*, **10**, 1 (1980).
7. M. J. Gillan, *J. Phys.*, **C7**, L1 (1974).
8. S. G. Brush, H. L. Sahlin, and E. Teller, *J. Chem. Phys.*, **45**, 2102 (1966).

9. J. P. Hansen, *Phys. Rev.*, **A8**, 3096 (1973).
10. Reference 7, and also private communication from M. P. Tosi.
11. Reference 4; see also for Lennard-Jones liquids Ref. 2.
12. V. A. Ivanov, I. N. Makarenko, A. M. Nikolaenko, and S. M. Stishov, *Phys. Letts.*, **47A**, 75 (1974); see also N. H. March and M. P. Tosi, *Atomic Dynamics in Liquids* (Macmillan: London), 1976).
13. E. P. Wigner, *Phys. Rev.*, **46**, 1002 (1934); *Trans. Faraday Soc.*, **34**, 678 (1938).
14. K. Fuchs, *Proc. Roy. Soc.*, **A151**, 585 (1935).
15. M. Ross, Proc. Grenoble (1980) Conference on "Liquid and amorphous metals."
16. D. K. Chaturvedi, G. Senatore, and M. P. Tosi. To appear in Nuovo Cimento Letters.
17. F. G. Edwards, J. E. Enderby, R. A. Howe, and D. I. Page, *J. Phys.*, **C8**, 3483 (1975): see also M. Parrinello and M. P. Tosi, *Rivista Nuovo Cimento*, 2, N.6 (1979).
18. J. Y. Derrien and J. Dupuy, *J. Physique*, **36**, 191 (1975).
19. E. W. J. Mitchell, P. J. Poncet, and R. J. Stewart, *Phil. Mag.*, **34**, 721 (1976).
20. See Ref. 18.
21. M. J. Gillan, B. Larsen, M. P. Tosi, and N. H. March, *J. Phys.*, **C9**, 889 (1976).
22. H. Reiss, S. W. Mayer, and J. L. Katz, *J. Chem. Phys.*, **35**, 820 (1961).
23. See Ref. 6; see also *Fast Ion Transport in Solids.* Editors: P. Vashishta, J. M. Mundy, and G. K. Shenoy (North-Holland: Amsterdam), 1979.
24. N. H. March, D. D. Richardson, and M. P. Tosi, *Solid State Commun.*, **35**, 903 (1980).
25. A. B. Lidiard, *Handbuch der Physik*, **20**, 246 (Springer: Vienna), 1957.
26. T. Kurosawa, *J. Phys. Soc. Japan*, **12**, 338 (1957).
27. N. H. March and M. P. Tosi, *Jour. Phys. Chem. Solids*, in press (1981).
28. C. R. A. Catlow, *Comments on Solid State Physics IX*, p. 157 (1980).
29. See Ref. 13: also N. H. March, W. H. Young, and S. Sampanthar, *The Many-Body Problem in Quantum Mechanics* (Cambridge: University Press), 1967.
30. C. M. Care and N. H. March, *Advances in Physics*, **24**, 101 (1975).
31. W. H. Young and N. H. March, *Phil. Mag.*, **4**, 384 (1959).
32. N. H. March, M. Suzuki, and M. Parrinello, *Phys. Rev.*, **B19**, 2027 (1979).
33. P. A. Egelstaff, N. H. March, and N. C. McGill, *Canadian J. Phys.*, **52**, 1651 (1974).
34. A. S. Brah, P. J. Dobson, N. H. March, B. A. Unvala, and L. Virdhee, *Inst. Phys. Conf. Series*, No. 41, Chap. 7, pp. 430–4 (1978); A. S. Brah, L. Virdhee, and N. H. March, *Phil. Mag.*, **B42**, 511 (1980).
35. S. Cusack, N. H. March, M. Parrinello and M. P. Tosi, *J. Phys.*, **F6**, 749 (1976).
36. P. J. Dobson, *J. Phys. C.*, **11**, L295 (1978).
37. M. Johnson, private communication.
38. N. H. March and M. P. Tosi, *Phys. Chem. Liquids* **10**, 113 (1980).

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