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LIQUID ALKALI METALS AND ALKALI-BASED ALLOYS  
AS ELECTRON-ION PLASMAS\*

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ABSTRACT

The article reviews the theory of thermodynamic and structural properties of liquid alkali metals and alkali-based alloys, within the framework of linear screening theory for the electron-ion interactions.

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## 1. Introduction

A liquid alkali metal can be viewed as a dense plasma of classical ions coupled to a nearly degenerate electron gas. In such a system near freezing, the strength of the bare ion-ion coupling is characterized by a value of the order of 200 for the ratio between the mean potential energy and the mean kinetic energy per ion. The corresponding ratio for the bare electron-electron coupling lies between 3 and 6, depending on the particular metal. A primitive model of the liquid metal can be constructed from the physical properties of its ionic and electronic components if they are assumed to be only weakly coupled.

In this viewpoint Bohm and Staver<sup>1</sup> calculated long ago the speed of sound in metals by screening the ionic plasma frequency  $\Omega_p = (4\pi q_z^2 e^2 / M)^{1/2}$  with the dielectric function of the electron gas in the long-wavelength limit,  $\epsilon(k) \rightarrow 1 + k_e^2 / k^2$ . The argument leads to long-wavelength phonons with an acoustic-type dispersion relation  $\omega(k) = [\Omega_p^2 / \epsilon(k)]^{1/2} \rightarrow ck$ , with a value  $c = (\frac{1}{3} Zm/M)^{1/2} v_F$  for the speed of sound when the inverse screening length  $k_e$  is estimated from the equation of state of the ideal Fermi gas,  $k_e = (6\pi q_e^2 / \epsilon_F)^{1/2}$ . This simple estimate of  $c$  is in reasonable agreement with experiment.

Many authors have developed this model in dealing with the phonon dispersion curves<sup>2</sup> and the cohesive properties<sup>3</sup> of alkali metals in the solid phase, and this work will be very briefly recalled in section 2. The model leads to the introduction of effective ion-ion pair potentials, that have subsequently been used with success<sup>4</sup> in computer simulation studies of metals in the liquid phase. In this scheme the liquid metal is effectively treated as a monatomic liquid, except that one should pay attention to the density dependence of the effective pair potential, arising from the underlying system of conduction electrons.

We are instead aiming here at presenting a viewpoint of liquid alkali metals which, in parallel with the solid-state work mentioned above, preserves explicitly their constitution as liquids of ions and electrons. The essential stimulus to the recent developments along this line has come from the progress made over the last decade in the understanding of classical ionic plasmas at high density.<sup>5</sup> The main emphasis will be on the thermodynamic and structural properties of the liquid alkali metals and their alloys, but a brief mention of other interesting alkali-based liquids will be made in the last section.

## 2. Some results of electron screening theory for crystalline metals

At the simplest level of discussion the electron-ion interaction is described by a model potential  $V_{ei}(r)$  that is supposedly sufficiently weak to be treated by lowest order perturbation theory. An ionic density fluctuation  $\rho_i(k, \omega)$  can then be viewed as an external disturbance on the homogeneous electron gas, which induces a polarization

$$\rho_e(k, \omega) = \chi_e(k, \omega) V_{ei}(k) \rho_i(k, \omega), \quad (2.1)$$

where  $\chi_e(k, \omega)$  is the linear density response function of the electron gas, related to its dielectric function by

$$\frac{1}{\epsilon(k, \omega)} = 1 + \frac{4\pi e^2}{k^2} \chi_e(k, \omega). \quad (2.2)$$

The adiabatic approximation for the electron-ion coupling is introduced by replacing  $\chi_e(k, \omega)$  in (2.1) by its static value  $\chi_e(k)$ . The total potential with which the ionic density fluctuation acts on an ion can thus be written

$$V_{ii}(k) \rho_i(k, \omega) + V_{ei}(k) \rho_e(k, \omega) \equiv V_{eff}(k) \rho_i(k, \omega), \quad (2.3)$$

which defines the effective ion-ion potential

$$V_{eff}(k) = V_{ii}(k) + \tilde{v}(k), \quad \tilde{v}(k) = \frac{V_{ei}^2(k)}{4\pi e^2/k^2} \left[ \frac{1}{\epsilon(k)} - 1 \right]. \quad (2.4)$$

as the sum of the bare ion-ion potential  $V_{ii}(k)$  (for which we shall take the Coulomb value  $4\pi Z^2 e^2/k^2$ ) and of the indirect term  $\tilde{v}(k)$  mediated by the conduction electron gas. The latter term is clearly dependent on the electron density  $\rho_e$ .

### 2.1 Phonon dispersion curves

The dynamical matrix of the metal can correspondingly be written, following Tóya<sup>2</sup>, as the sum of the dynamical matrix of a Coulomb lattice on an inert neutralizing background and of the contribution due to the indirect term  $\tilde{v}(k)$ . Many calculations of

phonon dispersion curves, with a variety of inputs for the bare electron-ion interaction and for the electronic dielectric function, have been carried out within this scheme, but we focus for the present purposes on the calculations of Price *et al*<sup>6</sup> for the alkali metals, noting for later reference the following main points:

(i) the phonon dispersion curves of each alkali metal can be rather accurately described with the simple one-parameter form proposed by Ashcroft<sup>7</sup> for  $V_{ei}(r)$ ,

$$V_{ei}(r) = \begin{cases} -Ze^2/r & \text{for } r > r_c \\ 0 & \text{for } r < r_c \end{cases} \quad (2.5)$$

or

$$V_{ei}(k) = -\frac{4\pi Ze^2}{k^2} \cos(kr_c). \quad (2.6)$$

The parameter in this expression is the 'core radius'  $r_c$ , at which a cut-off in the bare electron-ion Coulomb potential is introduced to mock up the effect of orthogonalization of the wave functions of the conduction electrons to the occupied core states. This simple scheme seems particularly appropriate for sodium and potassium, since the value of  $r_c$  obtained from the phonon dispersion curves agrees closely with values obtained from Fermi surface properties and from the liquid metal resistivity.

(ii) the role of the indirect interaction  $\tilde{v}(k)$  in bringing the dispersion curves from those of a bare Coulomb lattice to those of the metal is crucial for the longitudinal phonons (as shown by the Bohm-Staver argument: the LA branch emerges from a cancellation of the Coulomb singularities in the two terms of  $V_{eff}(k)$ ) but only minor for the transverse phonons, especially in the region of  $k$ -space around the Brillouin zone centre.

For a recent discussion of effective interionic potentials in metals, reference can be made to the review of Faber<sup>8</sup>.

## 2.2 Cohesive energy

The corresponding expression for the cohesive energy of a static ionic lattice screened by the electron gas consists of four terms<sup>3</sup>:

$$E = E_g + E_H + E_{es} + E_{bs}. \quad (2.7)$$

These are, respectively, the ground state energy  $E_g$  of the homogeneous electron gas on an inert background and its shift  $E_H$  (the 'Hartree' energy) due to the average non-Coulomb part of  $V_{ei}(r)$ ,

$$E_H = \rho_e \lim_{k \rightarrow 0} \left[ V_{ei}(k) + \frac{4\pi Z e^2}{k^2} \right] \quad (2.8)$$

( =  $2\pi \rho_e Z e^2 r_c^2$  for the Ashcroft potential);

the Madelung energy of the bare Coulomb lattice on an inert background,

$$E_{es} = -0.896 Z^2 e^2 (4\pi \rho_e / 3)^{1/3} \quad (\text{bcc lattice}); \quad (2.9)$$

and the 'band structure' energy due to the indirect ion-ion interactions,

$$E_{bs} = \frac{1}{2} \rho_e \sum_{\underline{G}(\neq 0)} \tilde{v}(\underline{G}) \quad (\underline{G} = \text{reciprocal lattice vectors}). \quad (2.10)$$

The equation of state, determining the equilibrium lattice parameter, and the bulk modulus of the metal follow from (2.7) by successive differentiations with respect to the ion density.

An important question is the 'thermodynamic consistency' of the theory, i.e. the equality between the value  $B$  of the bulk modulus derived from the cohesive energy and the value  $\tilde{B}$  obtained from the long-wavelength limit of the phonon dispersion curves. Even if the electronic dielectric function used in the calculations is thermodynamically consistent<sup>9</sup>, agreement between  $B$  and  $\tilde{B}$  requires the inclusion of non-linear effects of the electron-ion interactions.<sup>10</sup> The two values of the bulk modulus differ precisely in

that the expression for  $B$  contains an additional term arising from the density dependence of the effective ion-ion potential. The same term appears in the expression for  $\tilde{B}$  only when one keeps account also of the shift in average potential felt by the electrons, through a fourth-order perturbation calculation of the phonon dispersion curves.

At the level of the present discussion, therefore, the two approaches to the bulk modulus cannot be consistent. Good agreement with experiment for the cohesive properties of the crystalline alkalis, including the bulk modulus  $B$ , was nevertheless obtained in ref. 6 with the values of the core radius  $r_c$  derived from the phonon dispersion curves through an arbitrary increase of the value (2.8) for the Hartree energy by a factor 1.218.

## 3. Electron screening theory for liquid metals

We return to the discussion given at the beginning of section 2 and think of the ionic density fluctuation  $\rho_i(\underline{k}, \omega)$  as a polarization induced by a weak external potential  $V_i^{\text{ext}}(\underline{k}, \omega)$  fictitiously applied to the ionic system. In terms of linear response functions for the homogeneous fluid of ions and electrons we can write

$$\begin{cases} \rho_i(\underline{k}, \omega) = \chi_i(\underline{k}, \omega) V_i^{\text{ext}}(\underline{k}, \omega) \\ \rho_e(\underline{k}, \omega) = \chi_{ei}(\underline{k}, \omega) V_i^{\text{ext}}(\underline{k}, \omega) \end{cases} \quad (3.1)$$

Comparison with eqn (2.1) for weak electron-ion coupling yields in the adiabatic approximation

$$\chi_{ei}(\underline{k}, \omega) = \chi_e(\underline{k}) V_{ei}(\underline{k}) \chi_i(\underline{k}, \omega). \quad (3.2)$$

Under the same assumption of weak coupling between ions and electrons, we can also describe the ion fluid polarization  $\rho_i(\underline{k}, \omega)$  as that of a bare plasma responding to an internal potential which

is the sum of the external potential and of the potential due to the electron fluid polarization:

$$\varphi_i(k, \omega) = X_i^o(k, \omega) [V_i^{\text{ext}}(k, \omega) + V_{ee}(k) \varphi_e(k, \omega)]. \quad (3.3)$$

Comparison with (3.1) and (3.2) yields<sup>11</sup>

$$X_i(k, \omega) = X_i^o(k, \omega) / [1 - \tilde{v}(k) X_i^o(k, \omega)]. \quad (3.4)$$

In these expressions  $X_i^o(k, \omega)$  is the density response function of a bare ionic plasma on an inert background.

The zeroes of  $X_i^{-1}(k, \omega)$  give the longitudinal collective modes of the liquid metal. Their discussion on the basis of eqn (3.4) clearly parallels the theory of the phonon dispersion curves for the crystalline phase recalled in section 2.1. A connection with structural properties of the liquid can also be established from this equation in the static limit  $\omega \rightarrow 0$ , by virtue of the fluctuation-dissipation theorem<sup>12</sup> which for a classical fluid relates directly the static response to the structure factor describing the diffraction pattern of the liquid. One obtains for the structure factor  $S(k)$  of the liquid metal the expression<sup>13</sup>

$$S(k) = S_o(k) / [1 + \beta \varphi_i \tilde{v}(k) S_o(k)] \quad (\beta = 1/k_B T), \quad (3.5)$$

where  $S_o(k)$  is the structure factor of the one-component classical plasma (OCP) on an inert background. Similarly, eqn (3.2) yields for the ion-electron structure factor  $S_{ei}(k)$ , which describes the linearly distorted electron density around an ion in the liquid, the expression

$$S_{ei}(k) = (\varphi_i/\varphi_e)^{1/2} X_e(k) V_{ei}(k) S(k), \quad (3.6)$$

on the assumption that quantum effects can be neglected in this quantity. We shall here continue the discussion for alkali metals in parallel with section 2, and only later take up the calculation of their structure in the present scheme.

### 3.1 Compressibility by the method of long waves

The analysis of (3.4) in the limit of long wavelength and low frequency yields<sup>11</sup> longitudinal collective excitations with a dispersion relation appropriate to sound waves attenuated by viscosity. The value for the isothermal speed of sound agrees with that obtained from the liquid-metal compressibility  $K_T$  as derived directly from (3.5) through the use of the Ornstein-Zernike relation<sup>12</sup>,

$$\lim_{k \rightarrow 0} S(k) = \varphi_i k_B T K_T. \quad (3.7)$$

The latter approach involves the use of the long-wavelength form for the structure factor of the OCP,

$$\lim_{k \rightarrow 0} S_o(k) = \frac{k^2}{k_B^2} \left(1 + \frac{k^2}{k_B^2}\right)^{-1} \quad (k_B^2 = 4\pi\beta\varphi_i Z^2 e^2) \quad (3.8)$$

and leads to the result

$$\varphi_i k_B T K_T = \left(\frac{k_B^2}{k_e^2} + \frac{k_B^2}{k_i^2} + k_B^2 \epsilon^2\right)^{-1}. \quad (3.9)$$

The first term on the right-hand side is the Bohm-Staver result, but  $k_e$  now is the inverse screening length of the interacting electron gas. The other terms arise from the dispersion of the ionic plasma excitation and from the non-Coulombic term in the bare electron-ion interaction. The numerical results obtained<sup>14</sup> with the values of the core radius from the phonon analysis discussed in section 2.1 and the values of the 'inverse screening length'  $k_i$  of the OCP derived from its free energy<sup>15</sup> are reported in table 1. The good agreement with experiment shows that the theory is giving a consistent account of sound waves in the liquid and in the solid.

We also note that (3.6) in the long wavelength limit leads to<sup>16</sup>

$$\lim_{k \rightarrow 0} [S_{ei}(k) = Z(\varphi_i/\varphi_e)^{1/2} S(k)]. \quad (3.10)$$

In terms of the radial distribution functions  $g(r)$  and  $\varrho_{ie}(r)$  (see (3.12) and (3.13) below) this can be rewritten as

$$Z\varphi_i \int d\mathbf{r} [g(r) - 1] - \varphi_e \int d\mathbf{r} [\varrho_{ie}(r) - 1] = -Z \quad (3.10')$$

which expresses the condition that the total (ionic plus electronic) charge surrounding an ion must be equal to the negative of the charge of the ion (electroneutrality condition). A similar relation exists between the electron-electron structure factor in the liquid metal and  $S(k)$ .

### 3.2 Cohesive properties

The internal energy per ion in the liquid metal<sup>12</sup> can be written

$$E = T_i + T_e + \frac{1}{2e} \int d\mathbf{r} \left[ \rho_e^2 g_e(r) V_{ee}(r) + \rho_e^2 g(r) V_{ie}(r) + 2\rho_e \rho_i g_{ie}(r) V_{ie}(r) \right] \quad (3.11)$$

where  $T_i$  and  $T_e$  are the kinetic energies of ions and electrons in the metal, the  $V$ 's are the bare interaction potentials, and the  $g$ 's are the radial distribution functions, related to the structure factors by

$$S(k) = 1 + \rho_i \int d\mathbf{r} [g(r) - 1] \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (3.12)$$

(with a similar expression for  $g_e(r)$ ) and

$$S_{ie}(k) = (\rho_i \rho_e)^{1/2} \int d\mathbf{r} [g_{ie}(r) - 1] \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (3.13)$$

For weak electron-ion interactions we can consider the switching on of  $V_{ie}(r)$  as a process of polarization of the homogeneous electron gas by the ions in their fixed configuration as described by  $g(r)$ .

By a standard result of linear response theory, one-half of the energy gained by the interaction of the polarization with the polarizing field cancels against the 'quasi-elastic' energy spent in creating the polarization, i.e.

$$\frac{1}{2} \rho_e \int d\mathbf{r} [g_{ie}(r) - 1] V_{ie}(r) = E_p - T_e - \frac{\rho_e^2}{2e} \int d\mathbf{r} [g_e(r) - 1] V_{ee}(r) \quad (3.14)$$

Using (3.6) to eliminate  $g_{ed}(r)$ , the internal energy can thus be written

$$E = T_i + E_1 + E_2 + E_3 \quad (3.15)$$

where

$$E_1 = \frac{1}{2} \rho_e \int d\mathbf{r} g(r) V_{eff}(r), \quad (3.16)$$

$$E_2 = \frac{1}{2} [V_{eff}(r) - V_{ie}(r)]_{r=0}, \quad (3.17)$$

$$E_3 = E_p - \frac{1}{2} \rho_e \int d\mathbf{r} V_{eff}(r) + \rho_e \int d\mathbf{r} [V_{ie}(r) + \frac{Ze^2}{r}]. \quad (3.18)$$

The same expression was derived by Price<sup>17</sup> by direct analogy with eqns (2.7)-(2.10) for the solid. On the basis of the numerical results for the solid, Price added to (3.15) a shift of the Hartree energy by an amount  $0.218 E_H$  ( $E_H$  is the last term in (3.18)). His numerical results for the solid and liquid phases of sodium are reported in table 2:  $g(r)$  for the liquid was obtained from computer simulation.

Price also discussed the relation between the 'thermodynamic bulk modulus'  $B$  obtained from  $E$  (column 4 of table 2) and the 'dynamic bulk modulus'  $\tilde{B}$  obtained from (3.7) (column 5). The latter is equivalent to the bulk modulus of a conventional monatomic liquid in which the density dependence of the interactions is absent - so that, in particular, only the term  $E_1$  contributes, through the density dependence of  $g(r)$  and the  $r$  dependence of  $V_{eff}(r)$  - while  $B$  involves also the density dependence of the interactions.

### 4. Structure factor of liquid alkali metals

The use of eqn (3.5) at arbitrary wave number preliminarily requires a qualitative understanding and a quantitative theory of the structure of the OCF. The strength of the interactions in this model fluid, relative to the kinetic energy, is measured by the so-called plasma parameter  $\Gamma = Z^2 e^2 / (ak_B T)$  with  $a = (4\pi\rho_i/3)^{-1/3}$ . For liquid alkali metals near freezing, this parameter takes values

in the range 150-200. We are thus interested in the structure of the strongly coupled OCP.

#### 4.1 Structure of the OCP at strong coupling

Computer simulation work on the OCP shows<sup>18</sup> that at strong coupling the Coulomb correlation hole surrounding each point charge in the plasma is sharply defined, the radial distribution function  $g_0(r)$  being zero over a range of  $r$  comparable with  $\sigma$  and rising henceforth very sharply to reach its main peak in correspondence with the first-neighbour shell. This qualitative feature suggested to Gillan<sup>19</sup> the possibility of a theory in which the short-range correlations would be mocked up by endowing each point particle of the plasma with a hard-core diameter  $\sigma$ , such that  $g_0(r) = 0$  for  $r \leq \sigma$ . The imposition of this condition for  $r = \sigma$ , and not just for  $r < \sigma$ , serves to determine the value of  $\sigma$  as a function of  $\Gamma$  and is crucial from the thermodynamic point of view: it ensures that the hard cores remain fictitious and do not contribute to the virial pressure through hard-core collisions. This assumption on short-range correlations was combined by Gillan with an assumption on the long-range correlations due to the Coulomb interactions, for which he took, in essence, the Debye-Hückel approximation for  $r \gg \sigma$ .<sup>20</sup> These assumptions allow one to obtain an analytic solution for the structural problem, in the form of an analytic expression for  $S_0(k)$  in terms of parameters determined by the value of  $\Gamma$ :

The results of Gillan for the structure of the OCP are very promising, but the approach is not thermodynamically consistent, in the sense already mentioned in ref. 15 above: it violates the relation between  $k_1^2$  in (3.8) and the compressibility obtained from the free energy of the OCP. This approach has recently been

modified<sup>21</sup>, however, by allowing for deviations from the Debye-Hückel form of the correlations in the range  $r \gg \sigma$ , in such a manner as to embody thermodynamic consistency and the known equation of state, while retaining the advantage of an analytic solution for  $S_0(k)$ . An example of the accuracy attained by the theory is reported in figure 1 by comparison with computer simulation data at  $\Gamma = 160$ . The approach works with similar accuracy over a wide range of  $\Gamma$ , but seems to fail for  $\Gamma \lesssim 20$ : effects of penetration in the Coulomb hole are clearly indicated by computer simulation results at lower  $\Gamma$ 's ( $\lesssim 4$ ).

The qualitative point that we wish to stress again before proceeding is that the pair structure of the strongly coupled OCP is very closely described by that of a fluid of charged hard spheres, provided that the thermodynamic properties (the virial pressure, the free energy, and the 'compressibility sum rule') are preserved.

#### 4.2 Structure of liquid alkali metals

Equation (3.5) as it stands is not a useful formula to apply in the wave number region of the main peak of  $S(k)$ . This is most simply seen by noticing that the second term in the denominator is negative and attains here a magnitude of a few to several tenths of unity, with an uncertainty by a factor of order 4 as gauged from different forms for the bare electron-ion interaction that are available in the literature. The applicability of linear theory in this region of wave number, which corresponds to the first star of reciprocal lattice vectors in the crystal, is also open to serious question.

The simplest empirical modification that can be introduced in (3.5) is<sup>14</sup> to omit completely the screening correction for

wave number  $k$  above the first node of  $V_{ie}(k)$ , corresponding to  $k_n = \pi/(2r_c) \approx 2k_F$  for the Ashcroft potential in the alkali metals. This amounts to assuming that the structure factor of the liquid alkali metal coincides with that of the bare ionic plasma<sup>22</sup> for  $k \gg 2k_F$  and thus, according to the discussion given just above for the structure of the OCP, with that of a bare fluid of charged hard spheres. At lower wave numbers electron screening is instead allowed to intervene, ultimately leading for  $k \rightarrow 0$  to the behaviour discussed in section 3.1.

This simple empirical scheme yields very good agreement with the available experimental data for the structure of the alkali metals near freezing, although there is some indication (outside the likely uncertainty in the measured structure factors, which is not negligible in the region of the main peak of  $S(k)$ ) that some lowering of the value of  $\Gamma$  for the underlying bare plasma, below the value that would be appropriate to the temperature and density of the metal, may be needed for high quantitative accuracy. This is not a major matter, however, and indeed to a first approximation one may assert that the values of  $\Gamma$  for the alkali metals at freezing are all the same and equal to that value at which the OCP is believed to freeze<sup>23,24</sup>. This implies an approximate scaling law for the structure factors of the alkali metals at their respective freezing points, for  $k \gg 2k_F$ , since the structure factor of the OCP is a function only of  $ka$  at given  $\Gamma$ . The measured structure factors of liquid Na, K and Cs at freezing satisfy this scaling<sup>25</sup>.

We illustrate the merits of this approach by reporting in figure 2 the calculated temperature derivative of the structure factor of potassium near freezing against the X-ray diffraction results of Greenfield *et al.*<sup>26</sup>. The calculated temperature dependence arises from that of the structure factor of the OCP and (at wave numbers below  $1.2 \text{ \AA}^{-1}$ ) from thermal expansion effects in the

electronic screening. A similar comparison with neutron diffraction data<sup>27</sup> for the variation in position and height of the main peak with density in expanded rubidium is reported in figure 3. We stress that no adjustment of parameters is involved in these calculations and that in figure 3 and in the main part of figure 2 we are in fact comparing properties of a bare OCP with experimental data for a liquid metal.

##### 5. Thermodynamic properties of liquid alkali alloys by the method of long waves

The diffraction patterns of a binary mixture are described by three partial structure factors  $S_{\alpha\beta}(k)$ , related to the three radial distribution functions for the various types of atomic pairs. The extension of the Ornstein-Zernike relation (3.7) to multi-component liquids was given a long time ago by Kirkwood and Buff<sup>28</sup>. In terms of the direct correlation functions  $c_{\alpha\beta}(k)$ , defined through the inverse of the matrix of structure factors by

$$c_{\alpha\beta}(k) = \delta_{\alpha\beta} - S_{\alpha\beta}^{-1}(k), \quad (5.1)$$

the Kirkwood-Buff relations read

$$\lim_{k \rightarrow 0} c_{\alpha\beta}(k) = \delta_{\alpha\beta} - \frac{(\rho_{\alpha}\rho_{\beta})^{1/2}}{k_B T} \left( \frac{\partial \mu_{\alpha}}{\partial \rho_{\beta}} \right)_{T, V, \rho_{\beta}} \quad (5.2)$$

where  $\mu_{\alpha}$  is the chemical potential of the  $\alpha$ -th component and  $\bar{\alpha}$  denotes all the other components. For a binary alloy, in particular, the thermodynamic quantities in (5.2) can be related to its isothermal compressibility, to the coefficient for the dependence of the density on concentration, and to the 'concentration-concentration-structure factor'  $S_{cc}$ , given by the second derivative of the Gibbs free energy with respect to concentration  $c$  ( $c = c_2 = 1 - c_1$ ):

$$S_{cc} = N k_B T / \left( \frac{\partial^2 G}{\partial c^2} \right)_{T,P,N} \quad (5.3)$$

This quantity describes the correlations between thermodynamic fluctuations of concentration in the binary mixture, just as the Ornstein-Zernike relation relates the correlations between thermodynamic density fluctuations to the compressibility. Deviations of  $S_{cc}$  from its value for an ideal solution ( $S_{cc}^{\text{ideal}} = c_1 c_2$ ) thus measure the degree of relative ordering of the components of the mixture: an enhancement over  $S_{cc}^{\text{ideal}}$  reflects a tendency to segregation, while a depression reflects a tendency to 'alternation' of the components (sublattice formation).

We focus for the purposes of the present discussion on the Na-K alloy, for which all the necessary thermodynamic data have been available. Two main points have emerged from the analysis of these data:

(i) the ionic partial structure factors as functions of concentration<sup>29</sup> can be successfully fitted<sup>30</sup> by the model of conformal solutions; in which, in particular,  $S_{cc}$  has the expression

$$S_{cc} = c_1 c_2 / [1 - 2c_1 c_2 w / k_B T] \quad (5.4)$$

where  $w$  is the 'interchange free energy', a function of  $P$  and  $T$  but not of concentration;

(ii) the use of electroneutrality of the alloy allows one to relate<sup>31</sup> (as in eqn (3.10) for the pure metal) the partial structure factors involving the electronic component of the alloy to the ionic partial structure factors,

$$\lim_{k \rightarrow 0} [S_{\alpha\alpha}(k) = \left( \frac{\rho_{\alpha}}{\rho_e} \right)^{1/2} Z_{\alpha} S_{\alpha\alpha}(k) + \left( \frac{\rho_{\beta}}{\rho_e} \right)^{1/2} Z_{\beta} S_{\alpha\beta}(k)] \quad (5.5)$$

$S_{eNa}$  and  $S_{eK}$  are found to be strong functions of concentration, and specifically  $S_{eNa}$  increases rapidly with concentration, starting from either pure Na or pure K, while  $S_{eK}$  correspondingly decreases. In terms of the corresponding electron-ion radial distribution functions, this behaviour implies an electronic charge transfer from K

ions to Na ions in the alloying process, relative to a situation in which the electron distribution in the alloy is kept uniform.

Let us examine this problem from the point of view of electron screening theory. The extension of eqn (3.4) to the binary alloy<sup>11</sup> yields the following results:

(i) the dynamical modes of the screened two-component plasma at long wavelength and low frequency are<sup>11</sup>, in agreement with the prediction of linearized hydrodynamics, a sound wave mode attenuated by viscosity and by interdiffusion, as well as a relaxation mode of interdiffusion of the components;

(ii) the ionic partial structure factors are obtained<sup>14</sup> by inversion of eqn (5.1), where

$$c_{\alpha\beta}(k) = c_{\alpha\beta}^0(k) + \left( \frac{\rho_{\alpha} \rho_{\beta}}{\rho_e} \right)^{1/2} \frac{k^2 V_{\alpha\alpha}(k) V_{\beta\beta}(k)}{4\pi e^2 k_B T} [1 - 1/\epsilon(k)], \quad (5.6)$$

$c_{\alpha\beta}^0(k)$  being the direct correlation functions of the bare ionic plasma;

(iii) in particular for  $k \rightarrow 0$ ,

$$\left( \frac{\partial \mu_{\alpha}}{\partial \rho_{\beta}} \right)_{T,V,\rho_{\beta}} = \left( \frac{\partial \mu_{\alpha}}{\partial \rho_{\beta}} \right)_{T,V,\rho_{\beta}} + \frac{4\pi Z_{\alpha} Z_{\beta} e^2}{k^2} + 2\pi Z_{\alpha} Z_{\beta} e^2 (v_{\alpha\alpha}^2 + v_{\beta\beta}^2); \quad (5.7)$$

(iv) the electron-ion structure factors are given by<sup>32</sup>

$$S_{\alpha e}(k) = \chi_e(k) \left[ \left( \frac{\rho_{\alpha}}{\rho_e} \right)^{1/2} V_{\alpha e}(k) S_{\alpha\alpha}(k) + \left( \frac{\rho_{\beta}}{\rho_e} \right)^{1/2} V_{\beta e}(k) S_{\alpha\beta}(k) \right], \quad (5.8)$$

reducing to (5.5) for  $k \rightarrow 0$  where  $\chi_e(k) \rightarrow -k^2 / (4\pi e^2)$  and  $V_{\alpha e}(k) \rightarrow -4\pi Z_{\alpha} e^2 / k^2$ .

In examining the contact of the theory with the thermodynamic properties of the Na-K alloy through the Kirkwood-Buff formulae, it is useful to focus on  $S_{cc}$  since this quantity turns out to be extremely sensitive to the details of the theory. Equation (5.7) leads to an expression for  $S_{cc}$  of the form (5.4), with  $w$  given by

$$w/k_B T = \frac{1}{2} g \frac{(v_2 - v_1)^2}{k_T} + \frac{1}{2} (Z_1 - Z_2) k_B^2 \left[ v_1^2 - v_2^2 + (Z_1 - Z_2) (c_1 v_1^2 + c_2 v_2^2 - \chi_e^2) \right] \quad (5.9)$$

(the indices 1 and 2 refer to Na and to K, respectively).

The first term on the right-hand side, where  $v_2 - v_1$  is the difference in partial molar volumes of the components in the alloy,

clearly represents the elastic work in the alloying process. Its value can be obtained directly from experimental data, since

$$\varphi(v_2 - v_1) = -\frac{1}{\varphi} \left( \frac{\partial \varphi}{\partial c} \right)_{T,P,N} \quad (5.10)$$

This term alone is larger than the value of  $w$  obtained<sup>30</sup> from the conformal-solution analysis of the data ( $w/k_B T \approx 1.1$ ) by an order of magnitude.

The second term in (5.9), on the other hand, gives the electronic contribution in the alloying process and clearly vanishes for  $Z_1 = Z_2$ . The corresponding calculation of the electron-ion structure factors by (5.5) shows that the linear screening theory is completely missing the effect of electronic charge transfer from K to Na in alloying, that we have pointed out above. Similar conclusions have been illustrated recently<sup>33</sup> in relation to the formation of chemical bonding in semiconductors.

We have recently tried<sup>32</sup> to adjust empirically the formal results of screening theory for the Na-K alloy by allowing the ionic valences in the electron-ion interaction to vary with concentration. The crucial point is that, if one considers an isolated Na impurity in K metal, say, one would expect its electronic screening charge to be concentrated in a volume close to that of the sodium ion in sodium metal rather than in the average volume per ion of the dilute alloy. When this consideration is combined with the requirements that (i) the total number of conduction electrons is not varying with concentration, (ii) the valence of Na in Na metal is unity, and (iii) the valence shifts of the two components must balance at  $c = 1/2$ , one gets the simple relation

$$Z_1 = 1 + A c_2 \frac{c_1 v_1^0 + c_2 v_2^0}{v_1^0 + v_2^0}, \quad Z_2 = 1 - A c_1 \frac{c_2 v_1^0 + c_1 v_2^0}{v_1^0 + v_2^0} \quad (5.11)$$

where  $v_1^0$  and  $v_2^0$  are the volumes per atom of the pure components and  $A$  is a parameter.

The corresponding shift of core radii can be estimated in a first approximation by the relation

$$r_{c\alpha} Z_{\alpha} \approx \text{constant} \quad (5.12)$$

By introducing a second parameter in refinement of this relation, we have been able to fit with very high accuracy all the thermodynamic data for the Na-K alloy, namely  $K_T$ ,  $(\partial \varphi / \partial c)_{T,P,N}$  and  $S_{cc}$  as functions of concentration. The valence shifts are found to be small ( $\delta Z_{Na} \approx 0.2$  for an isolated Na impurity in K metal, decreasing with concentration to  $\delta Z_{Na} = 0$  in Na metal) but clearly crucial for the problem at hand. Calculations of partial structure factors at finite wave number, in relation to low-angle scattering data<sup>34</sup>, are now in progress.

## 6. Some other alkali-based liquids

We briefly mention in this concluding section two other types of liquid systems of special topical interest, whose theoretical treatment requires a detailed electron-ion model.

### 6.1 Solutions of molten alkali metals and molten alkali halides

The alkali metals and the alkali halides form true solutions in the liquid state, with partial miscibility at lower temperatures and a critical point above which the two liquids become miscible in any proportion<sup>35</sup>. The simultaneous presence of a critical point and of a metal-nonmetal transition is a special reason for interest in these systems.

At the metal-rich end of the phase diagram, the halogen X is believed<sup>36</sup> to be present in the solution as an  $X^-$  negative ion.

Its measured effect on the resistivity of the liquid metal<sup>37</sup> is large. Interesting questions are how such an ion is screened by the conduction electrons, the nature of its coordination shell of alkali ions, and the origin of the large contribution to the resistivity. Preliminary results have been obtained on this problem<sup>38</sup>.

At low metal concentrations the most interesting question concerns the nature of the states of the valence electrons of the alkali atoms added to the molten alkali halide. An electronic contribution to the conductivity in the concentration range 0.01-0.1 mol of metal has been approximately extracted from the experimental data<sup>37</sup>, and is found to be appreciable at these high temperatures and to increase with temperature. These features are qualitatively consistent with a phenomenon of Anderson localization.<sup>39</sup> At still lower concentrations (0.01 mol of metal or less) broad bands of optical absorption have been reported<sup>40</sup>, whose peak frequency and width are correlated with those of the F-centre absorption band in the alkali halide crystals. The existence of a bound electronic state analogous to the F centre in a molten alkali halide to which an alkali ion and a free electron have been added, with an excitation spectrum in approximate agreement with the observations, have been demonstrated.<sup>41</sup>

Extensive studies by neutron scattering techniques on some of these systems have been very recently reported by Jal<sup>42</sup>.

## 6.2 Cesium-gold alloy

The behaviour of the electric conductivity and of the optical absorption spectrum of this system<sup>43</sup> indicate that, at stoichiometric composition, it should be viewed as an 'ionic liquid' (or, better, as a strongly polar semiconducting liquid) composed of  $\text{Cs}^+$  and  $\text{Au}^-$

ions. As one moves away from stoichiometry by adding extra cesium, one thus expects qualitative similarities with the behaviour of alkali metal-alkali halide solutions near the salt-rich end of the phase diagram. The existence of localized electron states in a narrow range of concentration away from stoichiometry is indicated<sup>44</sup> by NMR data.

Extensive neutron diffraction data on this liquid alloy at various concentrations have been reported recently<sup>45</sup>. The behaviour of the diffraction pattern at low scattering angles shows qualitative changes occurring in the concentration range between 55% and 60% cesium. A shoulder in the diffraction pattern at  $k \approx 1.2 \text{ \AA}^{-1}$ , which can be associated with alternation of the components characteristic of an ionic liquid<sup>46</sup>, is replaced by a strong enhancement of the scattering for  $k \rightarrow 0$ , as in metallic alloys where the conduction electrons can screen the concentration fluctuations of the components. Work on the calculation of the structure of this alloy is in progress<sup>47</sup>.

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Table 1. Isothermal compressibility and temperature derivative of the speed of sound for liquid alkali metals near freezing  
(from D.K. Chaturvedi et al., ref. 14)

	Na	K	Rb	Cs	
$\epsilon_{1B}^{kTK_T}$ theory	0.0215	0.0231	0.0236	0.0235	
$\epsilon_{1B}^{kTK_T}$ expt	0.0233 <sup>a</sup>	0.0225 <sup>a</sup>	0.0220 <sup>a</sup>	0.0237 <sup>a</sup>	
	0.0240 <sup>b</sup>	0.0247 <sup>b</sup>			
$-(\partial c/\partial T)_P$ (m/secK)	theory	0.69	0.56	0.40	0.38
	expt <sup>(a)</sup>	0.52	0.53	≈ 0.4	≈ 0.3

(a) From G.M.B. Webber and R.W.B. Stephens, in 'Physical Acoustics' vol. IVB, p.53 (edited by W.P. Mason; Academic Press, New York 1968).

(b) From A.J. Greenfield et al., ref. 26.

Table 2. Equilibrium properties of sodium (in Rydberg/ion; from D.L. Price, ref. 17)<sup>a</sup>.

	$E_{\text{solid}}(\text{OK})$	$E_{\text{liquid}}$	$VP_{\text{liquid}}$	$VB_{\text{liquid}}$	$\sqrt{V}_{\text{liquid}}$
$T_i$	0.0010	0.0038	0.0025	0.0025	0.0025
$E_1$	-0.0160	-0.0114	0.0203	0.1030	0.0950
$E_2$	-0.2902	-0.2882	-0.0194	-0.0350	-
$E_3$	-0.1880	-0.1857	-0.0284	-0.0212	-
$\Delta E_H$	0.0308	0.0280	0.0280	0.0560	-
Total	-0.4624	-0.4535	0.0030	0.1053	0.0975
	$E_2 - E_3 = 0.0089$				
Expt	-0.460	0.00895	0.0000		0.0973
	± 0.002	± 0.00002			

(a) The liquid is at 393 K, i.e. close to freezing.

Figure captions

Figure 1. Structure factor of the OCP at  $\Gamma = 160$  (notice that the vertical scale has been enlarged by a factor 10 at low wavenumber). The dots are computer simulation results (ref. 18), while the curves are theoretical results based on the charged-hard-spheres model, without (dashed curve) and with (full curve) thermodynamic consistency. From D.K. Chaturvedi *et al*, ref. 21.

Figure 2. Temperature derivative of  $S(k)$  at constant pressure for liquid potassium near freezing, compared with X-ray diffraction data of Greenfield *et al* (ref. 26). From D.K. Chaturvedi *et al*, ref. 14.

Figure 3. Variation with density of the position (top) and height (bottom) of the main peak of  $S(k)$  for liquid rubidium, compared with neutron diffraction data of Block *et al* (ref. 27). From D.K. Chaturvedi *et al*, ref. 14.

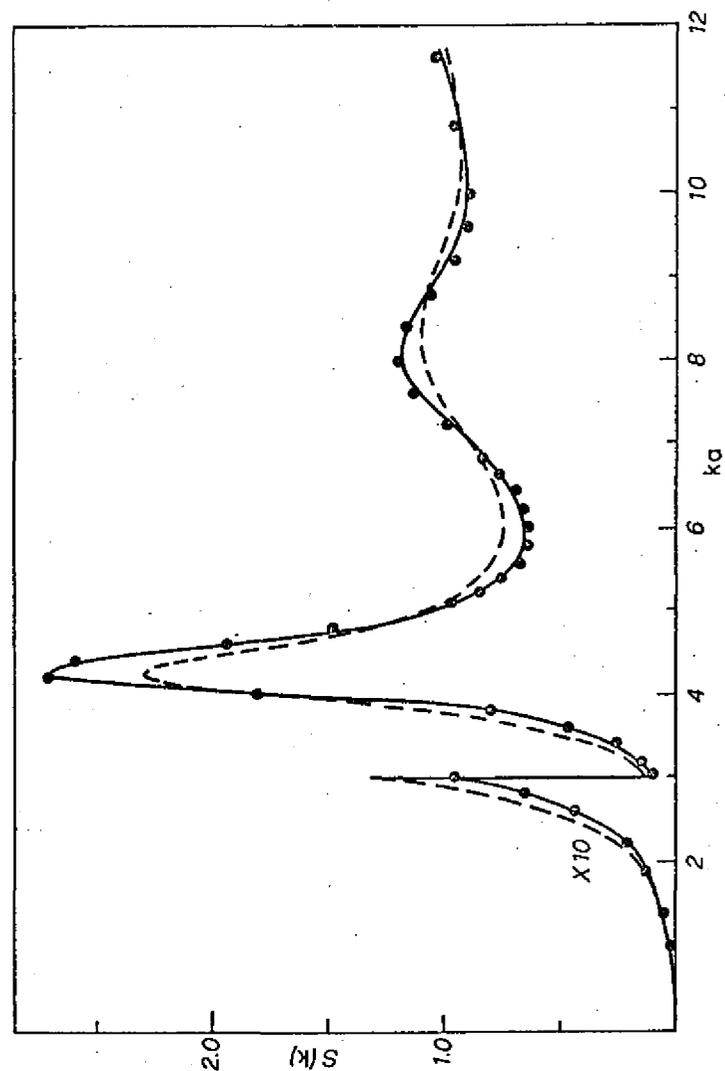


FIGURE 1.

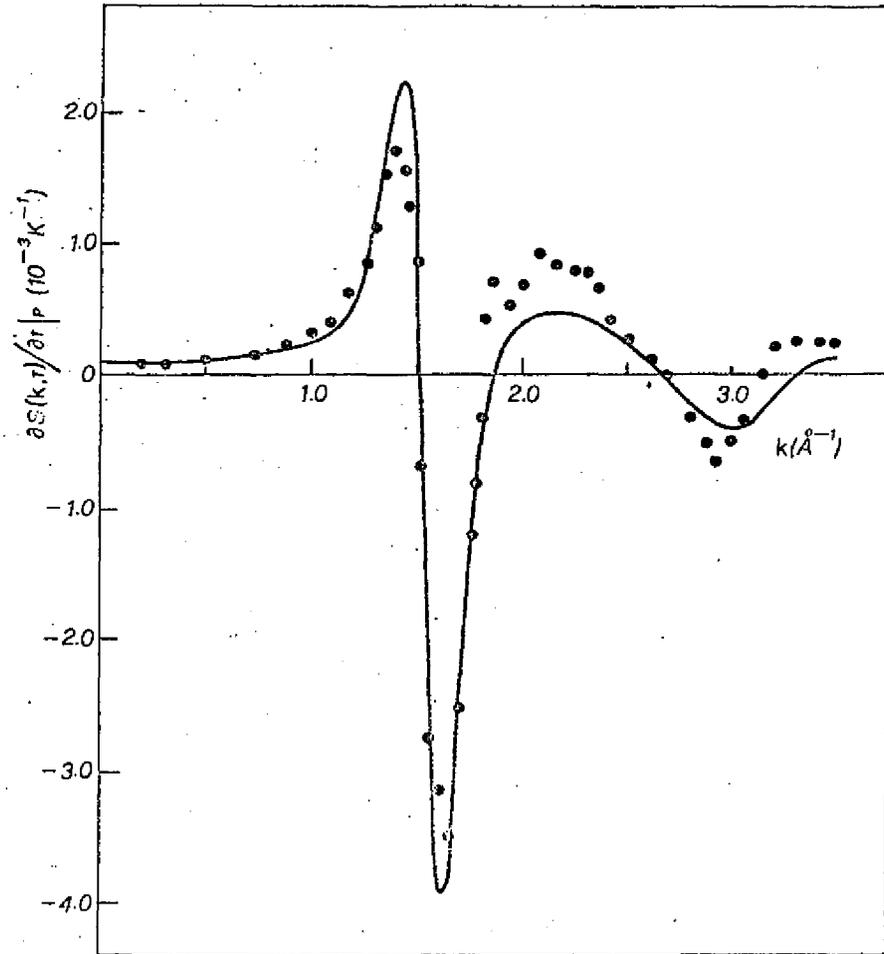


FIGURE 2.

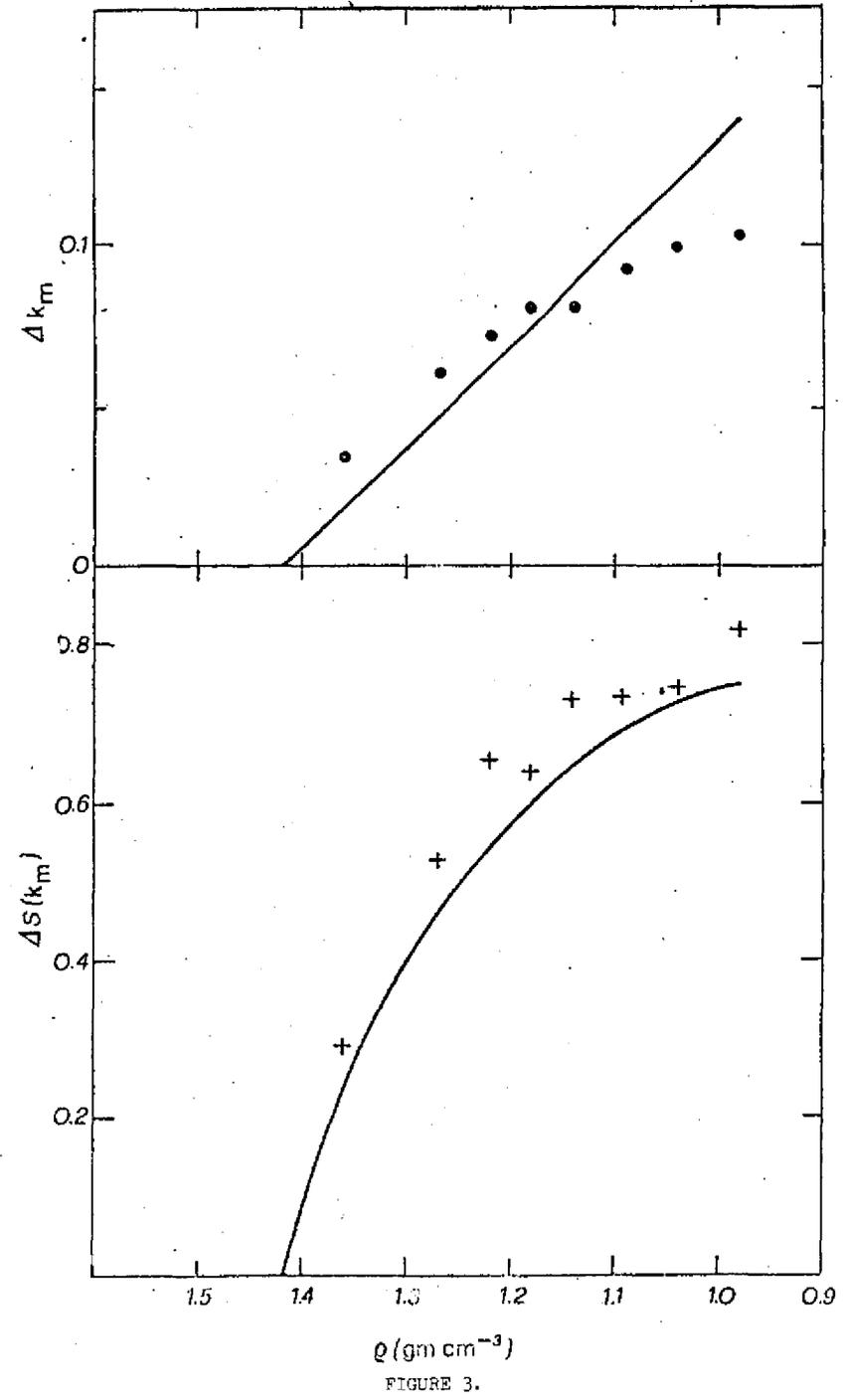


FIGURE 3.

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