ELECTRONIC VERSUS ATOMIC STRUCTURE IN LIQUIDS

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Résumé - Un modèle de sphères dures correspond assez bien au facteur de structure $S(q)$ d'un métal liquide. L'addition d'une contribution attractive augmente le $S(0)$ des sphères dures et modifie de façon négligeable les pics principaux. Une contribution répulsive annule $S(0)$ et produit des anomalies aux grandes valeurs de q . Ces résultats sont bien en accord avec les théories de pseudopotentiel. De plus, les modèles de mélange de sphères dures fournissent des indications sur le $S_{cc}(q)$ des alliages. Des contributions supplémentaires introduisent un potentiel d'ordre qui, s'il est attractif (ou répulsif), augmente (ou diminue) $S_{cc}(0)$ par rapport à la valeur des sphères dures et il y a tendance à une séparation de phase (formation de composés). Les théories de pseudopotentiel s'appliquent formellement mais introduisent des contributions où se concentrent les potentiels d'ordre ; les calculs ab initio sont évidemment risqués.

Abstract - Hard spheres provide a suitable reference fluid for liquid metal $S(q)$'s. Supplementary attractive tails enhance the hard sphere $S(0)$ and yields featureless principal peaks; repulsive tails suppress $S(0)$ and explain higher- q anomalies. These conclusions are consistent with NFE pseudopotential theory. Likewise, hard sphere mixtures provide insight into $S_{cc}(q)$ for an alloy. Supplementary tails define an ordering potential which, if repulsive (attractive), means $S_{cc}(0)$ is elevated (suppressed) relative to hard sphere values and there is a phase separating (compound forming) tendency. NFE pseudopotential theory formally applies but, even if valid, yields tails the inevitable errors in which accumulate in the ordering potential; ab initio calculation is evidently risky.

I - INTRODUCTION

The present paper, exceptionally at this conference on amorphous solids, concerns liquids. It shows how observed structure factors broadly delineate interatomic forces; this allows an assessment of how well the latter are specified by ab initio electron theory. It is interesting to note that structure factors depend on the full interatomic potentials in liquids and amorphous solids since all parts (excluding the impenetrable cores) are sampled and appear in the configurational averages. Crystals, on the other hand, are characterised by static lattice configurations and those nearby accessible by thermal vibration and so cannot, in principle, provide as much information.

Liquids and amorphous solids differ in that the former are in thermodynamic equilibrium whereas the latter are not. Thus, although the concept of the distribution function is used in both cases, only in the former is it governed by the principles of equilibrium statistical mechanics. This is of immense significance and help as is seen below.

We consider monatomic and binary metallic systems only. The former are of considerable intrinsic interest, illustrate some general principles and are, therefore, considered first (§II). Later, the binary problem is examined (§II) and a summary presented (§IV).

II - MONATOMIC FLUIDS

(i) Generalities

Consider a monatomic fluid of mean number density n . The radial distribution func-

tion $g(r)$ is obtainable from the interatomic forces using statistical mechanics and connection with experiment is made via the structure factor

$$S(q) = 1 + n \int \{g(r) - 1\} \exp(iq \cdot r) dr. \quad (1)$$

At long wavelengths, density fluctuation theory yields the identity

$$S(0) = n k_B T \kappa_T. \quad (2)$$

Here, κ_T is the isothermal compressibility and so $S(0)$ is measurable thermodynamically; it diverges as the critical point is approached.

The direct correlation function $c(r)$ is defined by the Ornstein-Zernike (OZ) equation

$$h(r) = c(r) + n \int h(|r - r'|) c(r') dr', \quad (3)$$

where $h(r) = g(r) - 1$. Alternatively, in Fourier transform, and using (1),

$$S^{-1}(q) = 1 - nc(q). \quad (4)$$

The direct correlation function reflects closely the potential; if the latter is pairwise and given by $v(r)$, statistical mechanics yields

$$c(r) \sim -v(r)/k_B T \quad (\text{large } r) \quad (4)$$

and experience suggests (5) is quite accurate anywhere outside the core. If $c(q)$ in (4) Taylor expands, we obtain the OZ form

$$S(q) = S(0)/(1 + \xi^2 q^2) \quad (\text{low } q). \quad (6)$$

Near the critical point, the correlation length, ξ , indicates the size of the density fluctuations; near the triple point, often (always in metals?) $S''(0) > 0$ with (formally) $\xi^2 < 0$.

Real fluids resemble, in zeroth order, hard sphere systems which have, therefore, been subject to much theoretical study. The results obtained will be drawn upon as required below.

(ii) The alkalis; illustrative example of Rb

Fig. 1 shows some observed structure factors /1/ for Rb. and their fit to hard sphere data. This is moderately satisfactory at large q but incorrect for small q , high T . Evidently, (6) applies in the latter circumstances, hard spheres alone being inappropriate.

The problem is simply solved thus: (a) calculate $v(r)$ (at each density) using pseudopotential theory, (b) separate core and tail parts /2/ (Fig. 2), (c) approximate the cores by hard spheres. (d) treat the tails as perturbations. The core scarcely varies with density and one reads off effective diameters σ using /4/ $v_{\text{core}}(\sigma) \approx k_B T$, the probing of the increasingly steep parts explaining the saturation noted in Fig. 1. The tails may be incorporated using the random phase approximation (RPA) /5/

$$c(r) = c_{\text{core}}(r) - n v_{\text{tail}}(r)/k_B T, \quad (7)$$

which recognises basic core and tail aspects (eq. (5)). Fourier transformation of (7) and use of (4) gives the Fig. 1 OZ behaviour.

A reverse analysis is also possible /6,7/; the observed $S(q)$ leads, using (4), to a $c(r)$ which, outside the core (cf. (5),(7)), yields a Fig. 2 tail.

Fig. 1 - Observed (—) and hard sphere fits (---) for $S(q)$ for Rb near saturation.

Fig. 2 - Core and tails (in mRy) for Rb at 350 K (1.46 g cm^{-3}) and 1500 K (0.64 g cm^{-3}) /3/.

(iii) Polyvalent metals; Waseda types.

We focus on the triple points. Here Waseda /10/ has identified three $S(q)$ types, mainly via the principal peak shapes (Fig. 3), and their distribution throughout the Periodic Table is as in Fig. 4. The sec. (ii) description for Rb offers an explanation for other type a cases which appears to be correct (see below) for groups 1A and 2A (excluding Be). An explanation /9,6/ for the others (although not the only one mooted) is that tails are essentially repulsive (eg. as used in (7)). Such a feature has been shown to underlie (depending upon detail) not only cases of type b and c, but also some of type a such as Pb /8,9/.

This viewpoint is consistent with recent systematically calculated pseudopotential results /10/ (Fig. 5) which, although inevitably open to quantitative revision, have the right general forms. For example, the pronounced minima in groups 1A and 2A are consistent with the observed closer packing in the solids while the loss of minimum allows possible, but not inevitable (cf. Pb), destabilisation to more open structures. Also, for liquids, as we have seen, such curves are suitable for explaining the Waseda classification. A detailed study /11/ lends credence to this view.

(iv) Low q limit of structure factors

We next show how the $S(0)$ values of Fig. 4 are qualitatively understood. Consider a reference fluid of hard sphere cores; then the attractive tail perturbations (Fig. 5) of the 1A, 2A elements enhance $S_{hs}(0)$ (cf. Rb, sec. (ii)) while the overall repulsive character of the others suppress it. Scrutiny of the data (Fig. 4) and the curves (Fig. 5) suggest $S_{hs}(0) \approx 0.020$ and it remains to understand this number.

Now the Gibbs-Bogoliubov method replaces the actual core by a truly 'all purpose' hard sphere with diameter given by /12/ $v_{core}(\sigma) \approx \frac{1}{2} k_B T$. This implies $\sim 45\%$ packing and $S(0) \approx 0.028$ - too large! But the subtler WCA method yields a 'squashy' sphere characterised essentially by a diameter σ and a force $v'_{core}(\sigma) / 4$. The criterion for σ becomes $v_{core}(\sigma) \approx \frac{1}{2} k_B T$ and the larger value thus produced combines with the force to describe $S(q)$ generally. However σ alone is appropriate to $q = 0$ and yields $S(0) \approx 0.020$ (corresponding to an apparent packing $(\pi/6)n\sigma^3 \approx 0.50$).

This account of $S(0)$ bears closer analysis, e.g. the increasing attractiveness of the tail (Fig. 5) through the sequence Hg, Cd, Zn, Mg, Ca, Sr, Ba is reflected in the $S(0)$ trend in Fig. 4 (Sr being, perhaps, a minor exception). Other correct

trends are discernable but numerical uncertainty suggests caution at this point.

III - BINARY MIXTURES

(i) Generalities

Consider a mixture of atoms, the partial number densities being $n_i \equiv c_i n$, where $c_1 = c$ and $c_2 = 1 - c$ are the concentrations. Then (1) generalises to

1A	2A	2B	3	4	5
Li BCC a 0.028	Be HCP		B		
Na BCC a 0.023	Mg HCP a 0.025		Al FCC a 0.017	Si DIA c	P
K BCC a 0.023	Ca FCC a 0.035	Zn HCP b 0.014	Ga ORC c 0.005	Ge DIA c	As RHL
Rb BCC a 0.022	Sr FCC a 0.031	Cd HCP b 0.012	In TET a 0.007	Sn TET c 0.007	Sb RHL c 0.019
Cs BCC a 0.024	Ba BCC a 0.036	Hg RHL b 0.005	Tl HCP a 0.011	Pb FCC a 0.009	Bi RHL c 0.010

Fig. 4(above) - Solid (room T) and liquid structures; also $S(0)$ at melting from eq. (2) and observed data. Some solid structures vary with T but the distinction between closer and looser packing persists.

Fig. 3(left) - Waseda $S(q)$ types: (a) hard sphere, (b) skew peak, (c) shouldered peak.

Fig. 5 - Hafner-Heine potentials (energies: $z^2 e^2 / R_a$; lengths: π / k_F). D_{op} = inter-atomic distance in close packed solid. Arrows denote liquid state diameters for 45% - 50% packing (scarcely distinguishable on this scale).

$$\tilde{S}_{ij}(q) = (n_i n_j)^{\frac{1}{2}} \left\{ g_{ij}(r) - 1 \right\} \exp(iq \cdot r) \quad (8)$$

where $\tilde{S}_{ij} = S_{ij} - \delta_{ij}$, and (3) becomes

$$h_{ij}(r) = c_{ij}(r) + \sum_k n_k \int h_{ik}(|\underline{r} - \underline{r}'|) c_{kj}(r') d\underline{r}' \quad (9)$$

where $h_{ij} = g_{ij} - 1$, and the c_{ij} so defined satisfy (cf. (5))

$$c_{ij}(r) \sim -v_{ij}(r)/k_B T \quad (\text{large } r) \quad (10)$$

Eqs. (9) transform (cf. (4)) to

$$\tilde{S}_{ij}(q) = (n_i n_j)^{\frac{1}{2}} c_{ij}(q) + \sum (n_k n_j)^{\frac{1}{2}} \tilde{S}_{ik}(q) c_{kj}(q). \quad (11)$$

Often, one stresses the concentration variable, c /13/. Consider /14/

$$g_{cc}(r) \equiv c_1^2 c_2^2 \{g_{11}(r) + g_{22}(r) - 2g_{12}(r)\} \quad (12)$$

which governs the concentration fluctuations; it is species-sensitive and indicates (by size and sign) the 'chemical short range order'. The corresponding structure factor is

$$S_{cc}(q) \equiv c_1 c_2 + n \int g_{cc}(r) \exp(iq \cdot r) , \quad (13)$$

for which (cf. (2)) there is a thermodynamic limit /13/

$$S_{cc}(0) = N k_B T / (\partial^2 G / \partial c^2)_{P,T,N} , \quad (14)$$

N being the total number of ions and G the Gibbs free energy.

Eq. (13) connects, via (12) and (8), to the c_{ij} /13/ to give

$$S_{cc}^{-1}(q) = (c_1 c_2)^{-1} - n \{c_{11}(q) + c_{22}(q) - 2c_{12}(q)\} - f(q) \quad (15)$$

where $f = f(c_{ij})$ is simple but longish so is not given here. Eq. (15) is the analogue of (4) and yields (cf. (6))

$$S_{cc}(q) = S_{cc}(0) / (1 + \xi^2 q^2) \quad (\text{low } q) \quad (16)$$

Just as $S(0)$ diverges at T_c , so does $S_{cc}(0)$ at phase separation (PS) and $S_{cc}^{-1}(0)$ on compound formation (CF). If $S_{cc}(0)$ is large (small) we have a PS(CF) tendency.

(ii) $S_{cc}(q)$ for some binary alloys

Fig. 6 shows three measured /14/ $S(q)$'s. That for the Ca alloy is close to hard sphere form (oscillating; near $c_1 c_2$) with diameters quite well decided externally

Fig. 6 - $S_{cc}(q)/c_1 c_2$ for the three alloys near melting.

$(q) \approx f(q)$ /13,15/ and $S_{cc}^{\text{core}}(q)$ $c_1 c_2$ to obtain

$$n \tilde{v}_{\text{ord}}(q) \approx \frac{1}{2} k_B T \{ (c_1 c_2)^{-1} - S_{cc}^{-1}(q) \}. \quad (19)$$

The general character described above follows when $q = 0$.

from pure liquid considerations. The others illustrate PS and CF tendencies; to interpret, we identify cores and tails and, in RPA (cf. (7)), write

$$c_{ij}(r) = c_{ij}^{\text{core}}(r) - n v_{ij}^{\text{tail}}(r) / k_B T \quad (17)$$

and find $S_{cc}(q)$ from (15). The result is governed by an ordering potential

$$v_{\text{ord}} = v_{12}^{\text{tail}} - \frac{1}{2} \{ v_{11}^{\text{tail}} + v_{22}^{\text{tail}} \}. \quad (18)$$

When, predominantly $v_{\text{ord}} \geq 0$, like (unlike) neighbour coordination is preferred and there is a PS(CF) tendency. This rule emerges by using (17), (18) in (15) and writing f_{core}

Ab initio calculation of the v_{ij} is risky both intrinsically (electron theory uncertainty) and because of error^{ij} accumulation in (18). Instead, Ratti and Bhatia /16/ chose hard sphere cores without tails for like ions, so $v_{12}^{\text{tail}} = v_{\text{ord}}$, by (18), and

$$v_{\text{ord}}(r) = \begin{cases} A & (r < \sigma_{12}) \\ A(\sigma_{12}/r)\exp\{-\lambda(r - \sigma_{12})\} & (r > \sigma_{12}) \end{cases} \quad (20)$$

With diameters externally specified and (arbitrarily) $\lambda = \sigma_{12}^{-1}$, the single adjusted parameter $A = 3.7 \times 10^{-3}$ eV accounts reasonably for Li - Na in Fig. 6. Conversely, transformation of (19) using observed data for $\text{Li}_{0.8}\text{Pb}_{0.2}$ leads /15/ to a similar picture with $A \approx -0.4$ eV, $\lambda = 1.1 \text{ \AA}$ and $\sigma_{12} \approx 3 \text{ \AA}$ (externally required and internally satisfied).

(iii) Low q limit of $S_{\text{cc}}(q)$

As in II(iv), $q = 0$ is of interest and some thermodynamically measured data are shown in Fig. 7. (Na - Cs is substituted for Li - Na since results for the latter are not known). Only

Fig. 7 - $S_{\text{cc}}(0)$ versus c . Ref. /18/ data interpolated by present writer.

$v_{\text{ord}} = \int v_{\text{ord}}(r) dr$, rather than the detail of (20), is needed and one finds that fixed externally prescribed diameters and $v_{\text{ord}} = 3.7 \text{ eV \AA}^3$ describes the whole curve quite well. But such a parametrisation fails for Li - Pb; e.g. the v_{ord} required at $c = 0.5$ is < 20% of that at 0.8 /19/.

The above, unfortunately, lacks a dependable electron basis. Pseudopotential theory, quite successful in §2 formally applies to alloys but, even if valid, the errors in finding the v_{ij} accumulate in v_{ord} . Here, clearly, much remains to be done.

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