

# Forces, structure and electronic correlation functions in liquid metals

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After a short discussion on the extraction of pair potentials from measurements of liquid structure, with the example of liquid Na near its freezing point, some examples of liquid metals under a wide range of thermodynamic conditions are considered. In particular, expanded fluid Cs and liquid H and D are referred to.

The nuclear structure factor  $S(k)$  is then considered in relation to its electronic correlation functions in liquid metals under conditions where a sharp separation can be made into core and valence electrons. Results on the valence electron-ion correlation function for liquid Mg and liquid Bi are reviewed and possibilities for seeing valence-valence electron pair correlations are mentioned.

Electrical resistivity theory is then treated in terms of a force-force correlation function, and the weak electron-ion interaction is found to be a limiting case, leading to the Bhatia-Krishnan-Ziman formula. However, for expanded Cs, one-body potential theory needs transcending and in doing so an inter-relationship between electrical resistivity and magnetic susceptibility is exposed. Some directions for future work are finally suggested.

## Background and a little history

WHEN Baskaran invited me to write an article for the special section, dedicated to the life and work of Krishnan, my mind went back to the special section in *Canadian Journal of Physics*<sup>1</sup>. The issue was dedicated to the memory of A. B. Bhatia, and my credentials for contributing to the present issue lie in the fact that Krishnan was the mentor of Avadh Bhatia. In the book, *Liquid Metals: Concepts and Theory*<sup>2</sup> are recorded two papers co-authored by Krishnan and Bhatia<sup>3,4</sup>; the first in *Nature* and the second in *Proc. R. Soc. (London)*. In the first of these were the seeds and more of what is nowadays usually referred to as the Ziman theory of the electrical resistivity of liquid metals. Ziman himself was not aware of the existence of the *Nature* article while creating his theory<sup>5</sup>. This is made clear by a late insertion in his MS of thanks to D. Shoenberg for drawing his attention to this reference. As to the second article, it seems fair to say that the very influential paper by Bhatia and Thornton<sup>6</sup> was motivated by the

1948 paper by Krishnan and Bhatia referenced above. Indeed, in the Bhatia-Thornton article the first two references are to the Krishnan-Bhatia studies of 1945 and 1948.

Thus, Krishnan was already well aware of the central importance of the liquid structure factor  $S(k)$ , essentially the Fourier transform of the radial distribution function  $g(r)$ , while developing the theory of liquid metals, and especially while considering its electronic transport properties. This awareness has led me to focus in this article on the theory of forces, structure and electronic correlation functions in liquid metals.

## Extraction of forces from liquid structure factor $S(k)$

Classical mechanical theories of liquid structure aim to calculate  $S(k)$ , or its  $\mathbf{r}$  space counterpart  $g(r)$ , from a given force law. Initially, theories were developed by Born and Green<sup>7</sup>, Percus and Yevick<sup>8</sup>, followed by the diagrammatic approaches used by several workers, leading to the so-called hypernetted chain (HNC) theory (see, for instance, the references in the article by Rushbrooke<sup>9</sup>).

Subsequently, Johnson and March<sup>10</sup> proposed to reverse the above approaches, and instead of attempting to calculate  $g(r)$  from a force law, they invoked experimental diffraction data for  $S(k)$  to extract a pair potential for liquid Na near its freezing point.

## Force equation for bulk homogeneous liquids

Though the electrons in liquid metals under normal conditions are almost completely degenerate, the nuclei can be treated classically. The pair correlation function  $g(r)$  of the nuclei, in terms of the potential of mean force  $U$  via the Boltzmann form, can be written as:

$$g(r) = \exp(-U(r)/k_B T), \quad (1)$$

where  $k_B$  denotes Boltzmann's constant.

The equation for the total force  $-\partial U(r_{12})/\partial \mathbf{r}_1$  - acting on atom 1 can be separated (i) into a direct part, arising from the assumed pair potential,  $\phi(r_{12})$ , between atoms

at separation  $r_{12}$ , and (ii) a part due to rest of the atoms. If a third atom is considered at position  $\mathbf{r}_3$ , clearly there is a need to introduce into the classical statistical mechanical theory a three-atom correlation function,  $g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ , that measures the probability of finding the three atoms simultaneously at  $\mathbf{r}_1$ ,  $\mathbf{r}_2$ , and  $\mathbf{r}_3$ .

This leads then, rather naturally, to write the so-called force equation (a member of the usual statistical mechanical hierarchy<sup>11</sup>) as:

$$\frac{-\partial U(r_{12})}{\partial \mathbf{r}_1} = \frac{-\partial \phi(r_{12})}{\partial \mathbf{r}_1} - \rho_1 \int \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_1} \frac{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g(r_{12})} d\mathbf{r}_3. \quad (2)$$

The last term has the form shown in eq. (2), since it has been asserted that there definitely are atoms at  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , and hence the three-body correlation function,  $g_3$ , must be divided by  $g(r_{12})$  to account for this. The number density,  $\rho_1$ , of the ions is present for essentially dimensional reasons.

It is in eq. (2) that Johnson and March<sup>10</sup> proposed to invert a 'measured'  $g(r)$  in a liquid metal, like Na, to find a pair potential  $\phi(r)$ . But they needed to 'decouple'  $g_3$  in terms of  $g(r)$ , leading thereby to the Born-Green theory already mentioned above. Currently, computer simulation<sup>12</sup> is being used to bypass the need for such 'uncontrolled' decoupling. This has thus led to the extraction of the so-called 'diffraction' potential for liquid Na near its freezing point as shown in Figure 1. The upper curve at large  $r$  is the pair potential obtained by Perrot and March<sup>13</sup> from density functional theory in the local density approximation. By including polarization interaction, Blazej and March<sup>14</sup> have shown that this theory curve will be pulled downwards towards the diffraction potential at sufficiently large  $r$ . It is remarkable that all the major features of the 'diffraction' potential studied by Reatto and co-workers<sup>12</sup> have been reproduced by the electron theory calculation of Perrot and March<sup>13</sup> as well, though quantitative differences remain.

### Liquid metals under a wide range of thermodynamic states

Following this study of liquid metal Na near freezing, in this section, we shall select a few topical examples of liquid metals under a wide range of thermodynamic conditions. We shall find it useful to begin with the expanded heavy alkalis, and in particular with Cs.

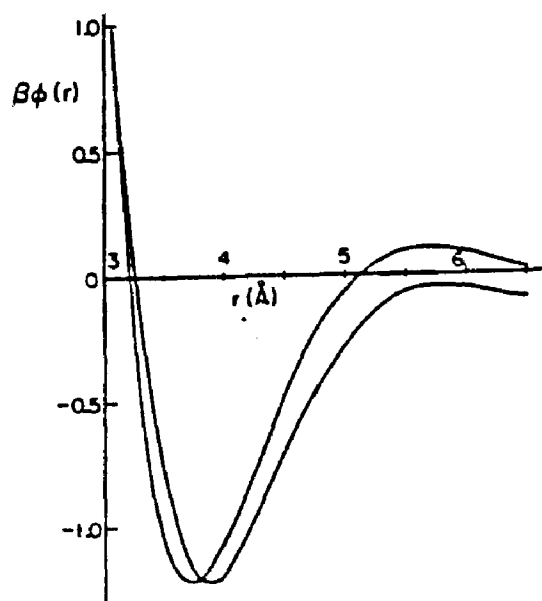
#### Expanded fluid Cs

It has been known for a long time that near freezing conditions, the so-called nearly-free electron model is

useful in describing the alkali metals, exception being Li. Having no  $p$  electrons in its core, this latter metal scatters conduction band electrons strongly and therefore behaves very differently from, Na, K, etc. But the pioneering work of Hensel *et al.* (see, reference by Winter *et al.*<sup>15</sup>), wherein neutron studies of the liquid structure factor  $S(k)$ , especially on Cs taken up the liquid-vapour coexistence curve towards the critical point, can leave no room to doubt that as the liquid density is reduced towards the critical density, the co-ordination number decreases rapidly while the near-neighbour distance remains remarkably constant. March<sup>16</sup> has shown that the results of Winter *et al.*<sup>15</sup> for the mass density  $d$  could be usefully represented in terms of the coordination number  $c$  by the linear relation

$$d = ac + b, \quad (3)$$

with  $a = 230$ , and  $b = -80$ , both in  $\text{kgm}^{-3}$ . This formula, admittedly by extrapolation to the critical density, yields approximately a coordination number of 2 for fluid Cs, and this has led to the proposal that in this fluid the critical point and the metal-insulator transition coincide, with the fluid undergoing a 'Peierls-type' distortion, as  $c$  reduces to 2 at the critical point. This invoking of chain structures at or near the critical density is interestingly related chemically to the low density forms of Rb and Cs, which on deposition on semiconductor surfaces form zig-zag chains. Freeman and March<sup>17</sup> have



**Figure 1.** Pair potentials for liquid metal Na near its freezing point, in units of  $\beta^{-1} = (k_B T)$ . Diffraction potential obtained by inverting liquid structure factor  $S(k)$  (see Reatto<sup>12</sup>) is shown in lower curve at large  $r$ . Electron theory potential calculated by Perrot and March<sup>13</sup> is shown in upper curve at large  $r$ . The work of Blazej and March<sup>14</sup> on polarization interaction lowers electron theory curve at sufficiently large  $r$ .

proposed some connection with the above critical point deductions, though these workers stress that the near-neighbour distance on the semiconducting substrates is fixed by the substrate geometry. It seems hard to escape the conclusion that chemical bonding plays a significant role in the heavy alkali fluids as the density is lowered towards the critical density.

Prompted by the above studies, density functional calculations have been made by March and Rubio<sup>18</sup> now, however, on long-range ordered assemblies of K atoms, with varying coordination numbers. The cohesive energy of these lattices,  $E(c, r_0)$  say, where  $r_0$  is the near-neighbour separation, can be interpreted on the basis of quantum-chemical model<sup>19</sup>, wherein only potential energy curves for the singlet ground state and the lowest triplet excited state of the  $K_2$  dimer in free space are invoked. This work on K has subsequently been extended to treat a variety of elements, from Bi to H, in low coordination configurations<sup>20</sup>. This prompts us to take H as a further example of liquid metals under extreme thermodynamic conditions.

However, before turning to H and D under extreme conditions of temperature and pressure, let us briefly consider forces and structure as discussed above. Following the structure factor measurements of Hensel *et al.* on expanded Cs (see ref. 15), Ascough and March<sup>21</sup> inverted a particular  $S(k)$  to extract a force law using the proposal of Johnson and March<sup>10</sup> discussed above, and their result is shown in Figure 2, where it is compared with the theoretical result obtained subsequently by Arai and Yokoyama<sup>22</sup>. There is thus a quantitative agreement between the 'diffraction' potential and theory, as in Figure 1, for Na near its freezing point.

### Liquid H and D

Significant progress in the ongoing search for metallic hydrogen has been made by Weir *et al.*<sup>23</sup>, using shock wave techniques. They found liquid metallic H as well as D at high temperatures for pressures in excess of 1.4 Mbar. Their experimental study on electrical conductivity showed results comparable with values available for expanded liquid Rb (see also the brief comments below).

Weir *et al.* interpreted the results of their experiments in terms of the presence of  $H_2$  molecules within the liquid metallic phase, thus paralleling earlier results on (now solid)  $I_2$ , though of course in quite a different range of thermodynamic states (see, for example, Siringo *et al.*<sup>24</sup>). These findings of Weir *et al.* have subsequently been challenged by a number of research groups. However, as March and Tosi<sup>25</sup> have stressed, none of these challenges is sufficiently convincing to overturn the original interpretation of Weir *et al.*<sup>23</sup>.

However, it is relevant in the present context to mention the path-integral Monte Carlo (QMC) investigation by Magro *et al.*<sup>26</sup> of isochoric heating of dense hydrogen. Following their results, March and Tosi<sup>27</sup> have modeled some aspects of their results and, in particular, the manner in which the electronic kinetic energy varies with density: (i) in an atomic-like high temperature H fluid, and (ii) in the low- $T$  molecular assembly. In regime (ii), the kinetic energy of localization, owing to containing a  $H_2$  molecule in a spheroidal box with infinite potential walls, was shown to have the basic fingerprints of the variation of the electronic kinetic energy with density of the plasma. As known from earlier studies, the infinite barrier imposed overestimates the localization behaviour, but March and Tosi<sup>27</sup> demonstrated that by softening the barrier (but now in the atomic fluid region) the results of Magro *et al.*<sup>26</sup> were reflected more quantitatively. March and Tosi<sup>25</sup> drew attention to the considerable interest of the above work on metallic hydrogen in its application to astrophysics. The discussion of the study by QMC of Magro *et al.* leads to the study of electronic correlation functions in liquid metals.

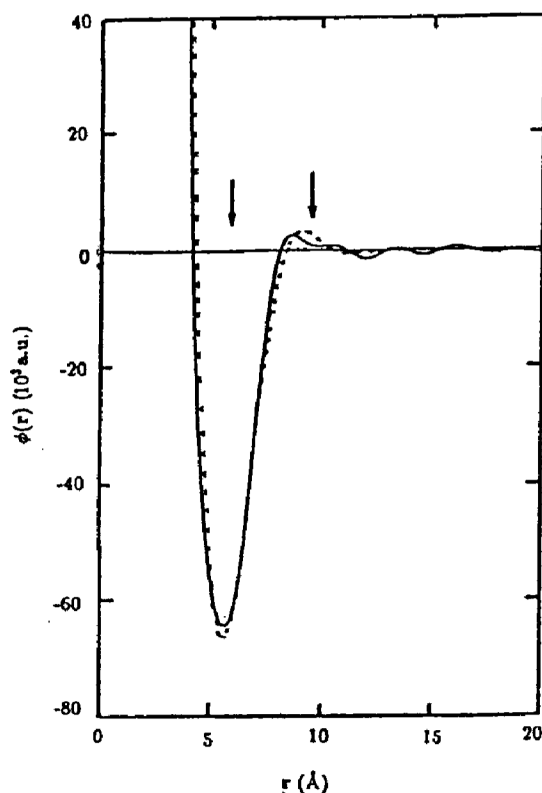


Figure 2. Pair potentials for expanded liquid metal Cs for atomic density of  $0.00416 \text{ \AA}^{-3}$  and temperature  $T = 1923 \text{ K}$ . Dashed line shows diffraction potential obtained by Ascough and March<sup>21</sup> by inversion of measured liquid structure factor  $S(k)$  (see e.g. Winter *et al.*<sup>15</sup>). Continuous line is due to Arai and Yokoyama<sup>22</sup>. After March and Rubio<sup>18</sup>.

## Electronic correlation functions: Experiment and theory

Following theoretical works of Chihara<sup>28</sup>, and Watabe and Hasegawa<sup>29</sup> in Japan, and March and Tosi<sup>30</sup> in Europe (actually the earliest study of which the present author is aware is that of Cowan and Kirkwood<sup>31</sup>, who used the forerunner of modern density functional theory; the Thomas–Fermi method), Egelstaff *et al.*<sup>32</sup> proposed a possible approach for extracting electronic correlation functions from 3 diffraction experiments: X-ray, neutron and electron studies. Unfortunately, progress in implementing their proposal has been slow, for reasons summarized, for instance, by Tamaki<sup>33</sup>.

The idea behind their approach is: a liquid metal, like Na, is a two-component system under conditions near freezing, consisting of Na<sup>+</sup> ions and electrons. Thus, just as for molten NaCl, three partial structure factors are required to define the structure of the liquid metal as well. The first, already discussed at some length above, is the nuclear–nuclear structure factor  $S(k)$ , best determined by neutrons (see, for example, the fairly recent study on liquid K near freezing by Johnson *et al.*<sup>34</sup>). Then assuming that the core electrons are attached to their own nuclei, two ‘electronic’ correlation functions are obtained, namely the valence–valence (vv) electron correlation function  $S_{vv}(k)$ , and the valence–ion correlation function  $S_{vi}(k)$ .

Though results for  $S_{vi}(k)$  have been obtained from experimental studies on this, substantial difficulties arise which have not yet been resolved. Therefore, a breakthrough came with the study of de Wijs *et al.*<sup>35</sup>, who used computer simulation to calculate  $S_{vi}(k)$  for liquid Mg and liquid Bi. It will be useful to introduce their work by considering the X-ray scattering from a simple liquid metal such as Na or Mg in this two-component theory of valence electrons and ions.

### X-ray scattering from simple s–p liquid metals

As set out by Egelstaff *et al.*<sup>32</sup>, the X-ray intensity  $I_x(k)$ , with  $k = (4\pi/\lambda) \sin(\theta/2)$ , where  $\theta$  measures the scattering angle and  $\lambda$  is the X-ray wavelength, can be expressed in terms of the total electron density,  $\rho(r)$ , as:

$$I_x(k) = V^{-1} \int d\mathbf{r} \, d\mathbf{r}' \langle \rho(r) \rho(r') \rangle \exp(i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')) \\ = F(\langle \rho(r) \rho(r') \rangle). \quad (4)$$

Here  $V$  is the volume of the sample while  $F$  is used to indicate the Fourier transform with respect to  $\mathbf{r} - \mathbf{r}'$ .

It is now of the essence of the approach to make the core–valence electron separation:

$$\rho(r) = \rho_c(r) + \rho_v(r), \quad (5)$$

and inserting this into eq. (4) yields

$$I_x(k) = F(\langle \rho_c(r) \rho_c(r') \rangle) + 2F(\langle \rho_c(r) \rho_v(r') \rangle) \\ + F(\langle \rho_v(r) \rho_v(r') \rangle). \quad (6)$$

But the core electron density is attached to its own nucleus, and therefore has the same ‘structure’ as the nuclei. The (rigid) core scattering factor  $f_c(k)$  is next introduced, with the property

$$\lim_{k \rightarrow 0} f_c(k) = Z_c = Z - z, \quad (7)$$

with  $Z_c$  the number of core electrons (e.g. 10 in liquid Mg). This is evidently related to atomic number  $Z$  and valence,  $z$ , as set out in eq. (7). Clearly the eq. (6) can be rewritten in terms of  $S(k)$  and  $S_{vi}(k)$  as:

$$I_x(k) = f_c^2(k) S(k) + 2f_c(k) S_{vi}(k) + F(\langle \rho_v(r) \rho_v(r') \rangle). \quad (8)$$

Let us turn now to relate this equation to theoretical models as well as to the computer studies of de Wijs *et al.*<sup>35</sup>.

### Weak electron–ion interaction and modelling of $S_{vi}(k)$

March and Tosi<sup>36</sup> in their book, (see also Rasolt<sup>37</sup>) present a model of  $S_{vi}(k)$  in terms of the nuclear structure factor  $S(k)$  in the case when the electron–ion interaction is weak (an appropriate assumption for one of the two metals, namely Mg, considered by de Wijs *et al.*<sup>35</sup>). This weak electron–ion interaction model yields for the ratio  $S_{vi}(k)/S(k)$  the result

$$\frac{S_{vi}(k)}{S(k)} = \frac{z^{1/2} v(k)}{(4\pi e^2/k^2)} \left( \frac{1}{\epsilon(k)} - 1 \right). \quad (9)$$

Here the ratio has been normalized so that the perfect screening condition (see the Appendix for a generalization to alloys)  $S_{vi}(0) = z^{1/2} S(0)$ , with  $z$  the valence (2 for Mg), is obeyed.

Elsewhere, March and Tosi<sup>38</sup> have evaluated this model with the simplest possible forms for each of its ingredients; namely (i) the bare electron–ion interaction  $\tau(k)$ , and (ii) the dielectric function  $\epsilon(k)$ . In their work, while the former is taken from the Ashcroft empty core model (Ashcroft<sup>39</sup>), the latter uses the Thomas–Fermi model. Returning to the Ashcroft model of (i), it is given in  $\mathbf{r}$  space by:

$$v(r) = \frac{-ze^2}{r} \quad r > R_c$$

$$= 0 \quad r \leq R_c, \quad (10)$$

the resulting Fourier transform yields:

$$v(k) = \frac{-4\pi ze^2}{k^2} \cos(kR_c). \quad (11)$$

For Mg, where the computer data of de Wijs *et al.*<sup>35</sup> was available for comparison, March and Tosi<sup>38</sup> took the core radius  $R_c$  as  $1.39a_0$ , while the electron-sphere radius  $r_s$  is  $2.66a_0$ , with  $a_0$  being the Bohr radius  $\hbar^2/me^2$ . Further, they inserted in eq. (9) the Thomas-Fermi dielectric constant corresponding to the screened Coulomb potential,  $(e^2/r) \exp(-k_{TF}r)$ , with  $k_{TF}^{-1}$ , the usual Thomas-Fermi screening length. This in turn is related to the Fermi wave number,  $k_F$ , by  $k_{TF}^2 = 4k_F/\pi a_0$ , which is equivalent to  $k_{TF} = 2.95(a_0/r_s)^{1/2} \text{ \AA}^{-1}$ . March and Tosi<sup>38</sup> thereby obtained in their modelling for the ratio of the valence-ion partial structure factor  $S_{vi}(k)$  to the nuclear structure factor  $S(k)$ , the following result:

$$\frac{S_{vi}(k)}{S(k)} = z^{1/2} (1 + (k/k_{TF})^2)^{-1} \cos(kR_c). \quad (12)$$

In Figure 3, taken from the work of March and Tosi<sup>38</sup>, this result of eq. (12) is plotted using values of  $R_c$  and  $k_{TF}$  appropriate to liquid Mg, namely  $R_c = 0.735 \text{ \AA}$  and  $k_{TF} = 1.81 \text{ \AA}^{-1}$ . As stressed by March and Tosi, it is to be noted from the computer data of de Wijs *et al.*<sup>35</sup> that the innermost node of  $S_{vi}(k)$  occurs near  $2.1 \text{ \AA}^{-1}$ , which is close to that given by the model result of eq. (12). They also pointed out that the deepest value of the ratio plotted is about  $-0.13$  from the model to

be compared with about  $-0.08$  at  $k_{min} \approx 2.5 \text{ \AA}^{-1}$  from the computer data. For a simple model, such as this, the agreement is quite satisfactory. March and Tosi<sup>38</sup> highlighted the point that the innermost node of both computer data and the model eq. (12) lies inside the  $k$  value corresponding to the principal peak of the nuclear structure factor  $S(k)$ . The deep negative region in  $S_{vi}(k)$  found by de Wijs *et al.*<sup>35</sup> is then in (anti)phase with the main peak in  $S(k)$ .

However, the Bi data of de Wijs *et al.*<sup>35</sup> is an example of strong electron-ion interaction and therefore the simple model above is not appropriate (for example, liquid Bi on freezing takes on semi-metallic character). Nevertheless, March and Tosi<sup>38</sup> have again computed the ratio  $S_{vi}(k)/S(k)$  from the computer results of de Wijs *et al.*<sup>35</sup>. The screening requirement, at  $k=0$ , now becomes, with valence 5,  $S_{vi}(0)/S(0) = 5^{1/2} = 2.24$  for the  $\text{Bi}^{5+}$  ionic state. The data shown in Figure 4 fall again, as for Mg, on a reasonably smooth curve. But the important difference from Mg (see March and Tosi<sup>38</sup>) is that the first node in  $S_{vi}(k)$  lies now at higher  $k$  than the principal maximum in  $S(k)$ . Hence  $S_{vi}(k)$ , for Bi, shows a positive peak in phase with the main peak in  $S(k)$  at  $k \approx 2 \text{ \AA}^{-1}$ .

#### Significance for electron-electron correlations of nodes in $S_{vi}(k)$

It is quite clear from the above discussion that the precise nodal structure of  $S_{vi}(k)$  is essential for quantitative work. For Bi, as March and Tosi point out, there are (at least) two nodes, at  $k_{oi}$  with  $i=1$  and 2, as is clear from Figure 4. But on the basis of eq. (8) for the X-ray intensity  $I_x(k)$ , it is clear that at  $k_{oi}$  this nodal

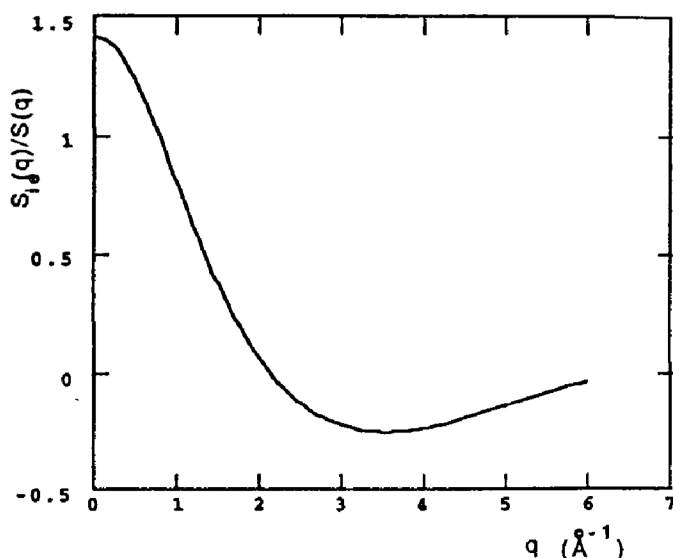


Figure 3. Ratio of electron (e)-ion (i) partial structure factor to  $S(k)$  for liquid Mg. After March and Tosi<sup>38</sup>.

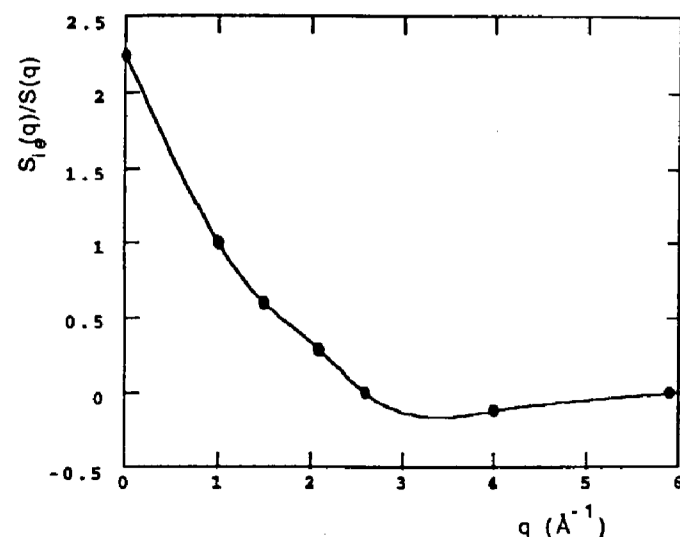


Figure 4. Same as in Figure 3, but now for liquid metal Bi near freezing, constructed from computer simulation of de Wijs *et al.*<sup>35</sup>; see March and Tosi<sup>38</sup>.

behaviour 'exposes' the valence-valence electron density correlations, provided the accuracy of the X-ray measurement can separate  $I_x(k_0)$  from  $f_c^2(k_0) S(k_0)$ .

Quantum chemical calculations can be used for estimating  $f_c(k)$  to high accuracy, whereas, as already mentioned,  $S(k)$  is directly accessible from neutron diffraction experiments. March and Tosi<sup>38</sup> refer to theoretical models of  $S_{vv}(k)$  but the interested reader should consult their paper for details (see also Magro *et al.*<sup>26</sup> for plots of the electron-electron pair correlation function in liquid H plasma).

### Electrical resistivity of expanded fluid metals: Force-force correlation function

Because of the crucial contribution of Krishnan to understanding of the electrical conductivity of liquid metals near their freezing points, it is therefore appropriate in this penultimate section to briefly review an approach to this property via a force-force correlation function (Rousseau *et al.*<sup>40</sup>). Their formula was initially criticized by a number of groups. But, provided one works with a completely degenerate electron assembly (see Leung and March<sup>41</sup> for  $T \neq 0$ ), these criticisms have been laid to rest by the demonstration<sup>42</sup> that this formula is a generalization of the impurity resistivity of a metal first correctly treated in a strong-scattering framework<sup>43</sup>. Apart from constants, which we have omitted here, the heart of the Huang formula is the sum  $S$  defined in terms of phase shifts  $\eta_l(k_F)$ :

$$S = \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l - 2l \sin \eta_l \sin \eta_{l-1} \cos(\eta_{l-1} - \eta_l), \quad (13)$$

which is readily shown to be equal to

$$S = \sum_{l=1}^{\infty} l \sin^2 (\eta_{l-1} - \eta_l). \quad (14)$$

Following the approach of the writer<sup>42</sup>, a result arrived at by Gerjuoy<sup>44</sup>, which was rediscovered by Gaspari and Gyorffy<sup>45</sup>, can now be used in eq. (14).

This then enables, for the case under discussion of the scattering of plane waves from a spherical potential  $V(r)$  of finite range, the sum  $S$  to be rewritten solely in terms of radial wave functions  $R_l(r)$  generated by  $V(r)$ , and the force  $-\partial V(r)/\partial r$ . The result is<sup>42</sup>:

$$S = \sum_{l=1}^{\infty} l \int_0^{\infty} dr_1 r_1^2 R_{l-1}(r_1) \frac{\partial V(r_1)}{\partial r_1} R_l(r_1) \\ \times \int_0^{\infty} dr_2 r_2^2 R_{l-1}(r_2) \frac{\partial V(r_2)}{\partial r_2} R_l(r_2). \quad (15)$$

At this point, connection must be established with the formula of Rousseau *et al.*<sup>40</sup>; see also McCaskill and March<sup>46</sup>. This has as its nub the force-force correlation function,  $F$ , again with unimportant multiplying factors suppressed:

$$F = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\partial V(\mathbf{r}_1)}{\partial \mathbf{r}_1} \cdot \frac{\partial V(\mathbf{r}_2)}{\partial \mathbf{r}_2} |\sigma(\mathbf{r}_1, \mathbf{r}_2)|^2, \quad (16)$$

where  $\sigma(\mathbf{r}_1, \mathbf{r}_2)$  denotes the energy derivative of the Dirac density matrix for potential  $V$  evaluated on the Fermi energy  $E_F = (\hbar^2 k_F^2 / 2m)$ . Analysing  $\sigma$  into partial waves for the central field case, with angular momentum components denoted by  $\sigma_l(r_1, r_2)$ , the integrand,  $f$ , in eq. (16), can be expressed in terms of this  $\sigma_l$  plus the force  $-\partial V/\partial r$ . Using this in the final step such that

$$\sigma_l(r_1, r_2) \propto R_l(r_1) R_l(r_2), \quad (17)$$

it is a straightforward matter to show that the formula<sup>43</sup>, rewritten in the form eq. (15), has precisely the same shape as the Rousseau *et al.*<sup>40</sup> formula. They are both force-force correlation functions of the type eq. (16).

### Relation to Bhatia-Krishnan-Ziman theory

The theory of Bhatia, Krishnan and Ziman (see e.g. Ziman<sup>47</sup>) is a weak scattering theory. The idea underlying this theory is to represent the total potential energy  $V(\mathbf{r})$  scattering the plane waves representing the conduction electrons by a sum of screened potentials  $v(\mathbf{r})$  at the ionic sites  $\mathbf{R}_i$ , where a 'snapshot' has been taken of the ions at a particular instant with:

$$V(\mathbf{r}) = \sum_i v(\mathbf{r} - \mathbf{R}_i). \quad (18)$$

Because the force-force correlation function  $F$  in eq. (16) already contains the potential energy  $V$  to second-order explicitly, this quantity  $F$  can be evaluated to second-order in  $V$  by replacing the energy derivative of the density matrix by its free electron (plane wave) value. Incorporating back all the numerical factors, the result for weak scattering with a sharp Fermi surface of  $2k_F$  can be obtained for the electrical resistivity  $R$  as:

$$R = \frac{3\pi}{\hbar e^2 v_F^2 \rho_i} \frac{1}{(2k_F)^4} \int_0^{2k_F} S(k) |v(k)|^2 4k^3 dk, \quad (19)$$

which is the formula of the Bhatia-Krishnan-Ziman theory. Here  $v_F$  is the Fermi velocity,  $\rho_i$  is the ionic number density, and since  $S(k)$ , as emphasized above, is accessible to experiment, the only quantity needed to find  $R$  is the Fourier transform of the localized atomic-like screened potential energy  $v(k)$ . Ziman was able to bring

the result eq. (19) to full fruition using pseudopotential theory for constructing  $v(k)$ .

The force-force correlation treatment has also been used to treat the extreme strong scattering limit, exemplified by the liquid rare earth metals, but we shall not go into details here.

### *Inter-relation between magnetic susceptibility and electrical resistivity in low density Cs*

To conclude this section on electrical resistivity, let us first note that the force-force correlation formula eq. (16) is a one-body potential theory. In the face of strong electron-electron correlations, this must be expected to break down and this has been made clear in the calculations of Ascough and March<sup>48</sup> on expanded Rb.

Such strong electron-electron correlations are, in fact fingerprinted in the magnetic susceptibility of expanded liquid metal Cs along the liquid-vapour coexistence curve (see, for example, Warren<sup>49</sup>). This has led the writer to report a treatment in which electrical resistivity is inter-related to magnetic susceptibility, and this is demonstrated in Figure 5, taken from March<sup>50</sup>. For the underlying theory, the work of Chapman and March<sup>51</sup> could be consulted, who utilize what is essentially heavy Fermion phenomenology at elevated temperatures. Their work, together with the subsequent study of the writer (March<sup>50</sup>) can leave no doubt that, in fluid Cs, as the critical point is approached both electron-electron and electron-ion interactions become strong, and it is in the interplay between them that the final solution of this problem will be found.

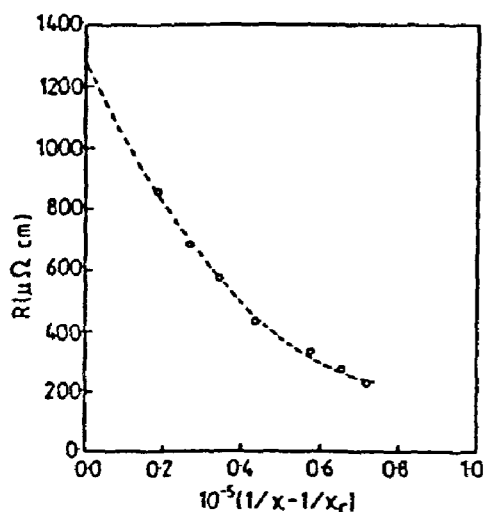


Figure 5. Marked correlation between experimental values of electrical resistivity  $R$  and reciprocal magnetic susceptibility  $1/\chi$  measured relative to its Curie limit (Warren<sup>49</sup>)  $1/\chi_c$  (after March<sup>50</sup>).

### **Summary and future directions**

For at least three liquid metals, Na and Be near their freezing points, and in expanded fluid Cs, force laws are now available which seem to be of high quality, though inevitably they are density-dependent and can only be invoked to discuss ionic rearrangements at constant volume. The Na potential has been brought into contact with density functional theory in the local density approximation<sup>13,52</sup>, and a similar density functional potential is available<sup>35,52</sup> for K and Be, though, in contrast to Na, these potentials have not yet been tested against diffraction potentials. For liquid Be, this has something to do with its toxicity. For expanded fluid Cs, the potential of Ascough and March<sup>21</sup> was obtained again by inverting the measured  $S(k)$  for a low density fluid state. The time seems ripe to extend this approach to other liquid metals occurring in a wide range of thermodynamic states.

This extraction of a force law has been followed by a discussion of local coordination in (i) the heavy alkalis Rb and Cs, and (ii) liquid H and D; for the latter, both shock wave and computer experiments are now available. The electron pair correlation function has been examined by Magro *et al.*<sup>26</sup>, and this has prompted a more general discussion of electronic correlation functions in liquid metals, with particular reference to Mg and Bi. Possible experiments which use computer calculations of the valence-ion correlation function  $g_{vi}(r)$ , or its corresponding partial structure factor  $S_{vi}(k)$  have been proposed by March and Tosi<sup>38</sup>, which may allow a window to the experimental observation of some parts of the valence-valence structure factor  $S_{vv}(k)$ .

Finally, because of the pioneering work of Bhatia and Krishnan<sup>3</sup> on electrical resistivity, some attention has been given to the force-force correlation treatment of electrical resistivity, which contains the Bhatia-Krishnan-Ziman theory as a limiting case. The inspiration given by the work of Krishnan to the development of a full understanding of structure and transport in liquid metals needs no further emphasis.

In discussing future directions, it would not be possible to avoid the conclusion that the static structure studies emphasized here need complementing by more work on the dynamical structure factor  $S(k, \omega)$ , which has the physical significance that it represents the probability that a neutron incident on the liquid metal will transfer momentum  $\hbar k$  and energy  $\hbar \omega$  to the liquid. Pioneering work on liquid Rb of this kind was that of Copley and Rowe<sup>53</sup>. This collective mode behaviour can be modeled somewhat as Feynman did for liquid He IV, and this model has been recently utilized<sup>54</sup> to discuss the ratio of bulk to shear viscosity. In turn, this leads to a relation between surface tension and shear viscosity, as re-emphasized recently especially by Egry<sup>55</sup>. And

since electrical conductivity and thermal conductivity are linked by the Wiedemann–Franz law, it is very much in the spirit of the present article to study why deviations<sup>56</sup> exist in liquid metals from this so-called ‘law’.

## Appendix

### Perfect metallic screening and electronic correlation functions in simple liquid metal alloys in the long wavelength limit

In the main text, screening conditions were used to relate nuclear–nuclear and valence electron–ion correlation functions to the valence of the liquid metal in question<sup>28,29</sup>. In the context of this article, it seemed appropriate to give in this appendix the generalization of these conditions by Bhatia *et al.*<sup>57</sup> to the case of a binary liquid metal alloy (e.g. Na–K).

The argument of Bhatia *et al.*<sup>57</sup> can be summarized as follows. Suppose that ions of types A and B have valences of  $z$  and  $Z$  respectively. Six distinct correlation functions,  $S_{AA}$ ,  $S_{BB}$ ,  $S_{vv}$  and cross-correlation functions  $S_{vA}$ ,  $S_{vB}$ , and  $S_{AB}$  are required to characterize the structure of the mixture of A, B and valence electrons  $v$ . Let us set out the condition of perfect screening (compare the non-degenerate case of Debye–Hückel theory with the totally degenerate electron assembly considered here).

The idea is then to view the surrounding charge density first from an A ion, then from a B ion, etc. For the case of the A ion, the positive charges  $ze$  are distributed at a distance  $r$  from the ion chosen as origin, with charge density  $ze\rho_A g_{AA}(r)$ , ions with charge  $Ze$  with density  $Ze\rho_B g_{AB}(r)$  and valence electrons with charge density  $-e\rho_v g_{vA}(r)$ ,  $\rho_A$ ,  $\rho_B$ , and  $\rho_v$  being the number densities of the three species. The total charge density when viewed from an ion A must clearly integrate to  $-ze$  for perfect screening, since long-range electric fields cannot exist in a conducting medium. Thus one can write

$$-ze = ze\rho_A \int (g_{AA}(r) - 1) d\mathbf{r} + Ze\rho_B \int (g_{AB}(r) - 1) d\mathbf{r} - e\rho_v \int (g_{vA}(r) - 1) d\mathbf{r}, \quad (\text{A1})$$

where unity has been subtracted from each of the  $g$ ’s for convergence at infinity. This can be achieved trivially, as shown, since

$$ze\rho_A + Ze\rho_B = e\rho_v. \quad (\text{A2})$$

Similar equations to (A1) follow by sitting next on a B ion and then on a valence electron.

Next, one defines partial structure factors in the long wavelength limit  $k$ , which tends to zero, by

$$S_{ij} = \delta_{ij} + (\rho_i \rho_j)^{1/2} \int (g_{ij}(r) - 1) d\mathbf{r}. \quad (\text{A3})$$

Then the screening equations referred to above, of which eq. (A1) is an explicit example, can be shown to take the form (Bhatia *et al.*<sup>57</sup>):

$$S_{vv} = z^2 \left( \frac{\rho_A}{\rho_v} \right) S_{AA} + 2zZ \frac{(\rho_A \rho_B)^{1/2}}{\rho_v} S_{AB} + Z^2 \left( \frac{\rho_B}{\rho_v} \right) S_{BB}, \quad (\text{A4})$$

$$S_{vA} = \left( \frac{\rho_A}{\rho_v} \right)^{1/2} \left\{ zS_{AA} + ZS_{AB} \left( \frac{\rho_B}{\rho_A} \right)^{1/2} \right\}, \quad (\text{A5})$$

and

$$S_{vB} = \left( \frac{\rho_B}{\rho_v} \right)^{1/2} \left\{ zS_{AB} + Z \left( \frac{\rho_A}{\rho_B} \right)^{1/2} S_{BB} \right\}. \quad (\text{A6})$$

Using experimental data of McAllister and Turner<sup>58</sup>, Bhatia *et al.*<sup>57</sup> have plotted  $S_{vv}$ , etc. as functions of concentration for the liquid Na–K system ( $z=Z=1$ ). The interested reader should refer to their Figure 1 and to a subsequent review by Tamaki<sup>33</sup>. More recent work by March and Tosi<sup>38</sup> has also utilized these screening relations in connection with studies on Li–H plasma.

1. March, N. H. and Singh, R. N., *Can. J. Phys.*, 1987, **65**, 219.
2. March, N. H., *Liquid Metals: Concepts and Theory*, Cambridge University Press, Cambridge, 1990.
3. Bhatia, A. B. and Krishnan, K. S., *Nature*, 1945, **156**, 503.
4. Bhatia, A. B. and Krishnan, K. S., *Proc. R. Soc. London Ser. A*, 1948, **194**, 185.
5. Ziman, J. M., *Philos. Mag.*, 1961, **6**, 1013.
6. Bhatia, A. B. and Thornton, D. E., *Phys. Rev.*, 1970, **B2**, 3004.
7. Born, M. and Green, H. S., *Proc. R. Soc. London Ser. A*, 1946, **188**, 10.
8. Percus, J. K. and Yevick, G. J., *Phys. Rev.*, 1958, **110**, 1.
9. Rushbrooke, G. S., *Physica*, 1960, **26**, 259.
10. Johnson, M. D. and March, N. H., *Phys. Lett.*, 1963, **3**, 313.
11. Hill, T. L., *Statistical Mechanics*, McGraw-Hill, New York, 1956.
12. Reatto, *Philos. Mag.*, 1998, **95**, 353.
13. Perrot, F. and March, N. H., *Phys. Rev.*, 1990, **A41**, 4521.
14. Blazej, M. and March, N. H., *Phys. Rev.*, 1993, **E48**, 1782.
15. Winter, R., Pilgrim, W. C. and Hensel, F., *J. Phys. Condens. Matter*, 1994, **A245**, 6.
16. March, N. H., *J. Math. Chem.*, 1990, **4**, 271.
17. Freeman, G. R. and March, N. H., *J. Phys. Chem.*, 1994, **98**, 9486.
18. March, N. H. and Rubio, A., *Phys. Rev.*, 1997, **B56**, 13865.
19. March, N. H., Tosi, M. P. and Klein, D. J., *Phys. Rev.*, 1995, **B52**, 9115.
20. March, N. H. and Rubio, A., *Phys. Stat. Solidi*, 1998, in press.
21. Ascoug, J. and March, N. H., *Phys. Chem. Liquids*, 1990, **21**, 251.
22. Arai, T. and Yokoyama, I., *Phys. Chem. Liquids*, 1993, **26**, 143.
23. Weir, S. T., Mitchell, A. C. and Nellis, W. J., *Phys. Rev. Lett.*, 1996, **76**, 1860.
24. Siringo, F., Pucci, R. and March, N. H., *High Pressure Rev.*, 1989, **8**, 10.
25. March, N. H. and Tosi, M. P., *Plasma ions*, 1998, **16**, 71.



26. Magro, N. R., Ceperley, D. M., Pierleoni, C. and Bernu, B., *Phys. Rev. Lett.*, 1996, **76**, 1240.
27. March, N. H. and Tosi, M. P., *Nuovo Cim.*, 1996, **18D**, 1661.
28. Chihara, J., in *The Properties of Liquid Metals* (ed. Takeuchi, S.), Taylor and Francis, London, 1973, 13.
29. Watabe, M. and Hasegawa, M., *The Properties of Liquid Metals* (ed. Takeuchi, S.), Taylor and Francis, London, 1973, 13.
30. March, N. H. and Tosi, M. P., *Ann. Phys.*, 1973, **81**, 414.
31. Cowan, R. D. and Kirkwood, J. G., *J. Chem. Phys.*, 1958, **29**, 264.
32. Egelstaff, P. A., March, N. H. and McGill, N. C., *Can. J. Phys.*, 1974, **52**, 1651.
33. Tamaki, S., *Can. J. Phys.*, 1987, **65**, 288.
34. Johnson, M. W., March, N. H., Perrot, F. and Ray, A. K., *Philos. Mag.*, 1994, **B69**, 965.
35. de Wijs, G. A., Pastore, C., Selloni, A. and van der Lugt, W., *Phys. Rev. Lett.*, 1995, **75**, 4480.
36. March, N. H. and Tosi, M. P., *Coulomb Liquids*, Academic Press, New York, 1984.
37. Rasolt, M., *Phys. Rev.*, 1985, **B31**, 1615.
38. March, N. H. and Tosi, M. P., *Lasers and Particle Beams*, 1998, in press.
39. Ashcroft, N. W., *J. Phys.*, 1968, **C1**, 232.
40. Rousseau, J. S., Stoddart, J. C. and March, N. H., *J. Phys.*, 1972, **C5**, L175.
41. Leung, C. H. and March, N. H., *Plasma Phys. (GB)*, 1977, **11**, 277.
42. March, N. H., *Philos. Mag.*, 1975, **32**, 497.
43. Huang, K., *Proc. Phys. Soc.*, 1948, **60**, 161.
44. Gerjuoy, E., *J. Math. Phys.*, 1965, **6**, 993.
45. Gaspari, G. D. and Gyorffy, B. L., *Phys. Rev. Lett.*, 1972, **28**, 801.
46. McCaskill, J. S. and March, N. H., *J. Phys. Chem. Solids*, 1984, **45**, 215.
47. Ziman, J. M., *Adv. Phys.*, 1964, **13**, 89.
48. Ascough, J. and March, N. H., *Phys. Chem. Liquids*, 1991, **23**, 37.
49. Warren, M. M., *Phys. Rev.*, 1984, **329**, 7012.
50. March, N. H., in *Recent Developments in the Physics of Fluids* (eds Howells, W. S. and Soper, A. K.), IOP, Bristol, 1992, p. 189.
51. Chapman, R. G. and March, N. H., *Phys. Rev.*, 1988, **B38**, 792.
52. Perrot, F. and March, N. H., *Phys. Rev.*, 1990, **A42**, 4884.
53. Copley, J. R. D. and Rowe, J. M., *Phys. Rev. Lett.*, 1974, **32**, 49.
54. March, N. H. and Alonso, J. A., *Mol. Phys.*, 1998, **95**, 353.
55. Egry, I., *Scr. Metall. Mat.*, 1993, **28**, 1273.
56. March, N. H. and Tankeshwar, K., *Phys. Chem. Liquids*, 1997, communicated.
57. Bhatia, A. B., March, N. H. and Tosi, M. P., *J. Phys.*, 1973, **C6**, L59.
58. McAlister, S. P. and Turner, R., *J. Phys.*, 1972, **F2**, L51.

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## K. S. Krishnan and early experimental evidences for the Jahn–Teller theorem

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**Jahn–Teller theorem**, proposed in 1937, predicts a distortional instability for a molecule that has symmetry based electronic degeneracy. In 1939, Krishnan emphasized the importance of this theorem for the arrangement of water molecules around the transition metal or rare earth ions in aqueous solutions and hydrated salts, in a short and interesting paper published in *Nature* by pointing out at least four existing experimental results in support of the theorem. This paper of Krishnan has remained essentially unknown to the practitioners of Jahn–Teller effect, even though it pointed to the best experimental results that were available, in the thirties and forties, in support of Jahn–Teller theorem. Some of the modern day experiments are also in conformity with some specific suggestions of Krishnan.

JAHN–TELLER effect<sup>1</sup> is a beautiful and simple quantum phenomenon that occurs in molecules, transition metal complexes as well as solids containing transition metal

or rare earth ions. It states roughly that ‘a localized electronic system that has a symmetry-based orbital degeneracy, will tend to lift the degeneracy by a distortion that results in the reduction of the symmetry on which the degeneracy is based’. In isolated systems such as a molecule or a transition metal complex it is a dynamical or quasi static phenomenon. They are called dynamic and static Jahn–Teller effects<sup>2</sup>. When it occurs co-operatively in crystals it is a spontaneous symmetry breaking phenomenon and a crystal structure change. This is called a co-operative Jahn–Teller effect.

Even before Jahn–Teller theorem appeared, Krishnan and collaborators<sup>3</sup> performed a series of pioneering magneto crystalline anisotropy study of families of paramagnetic salts containing transition metal and rare earth ions lending good support to various new quantum mechanical ideas including those of Bethe, Kramers and Van Vleck on crystal field splitting and magneto crystalline anisotropy. In the biographical Memoirs of the Royal Society of London, K. Lonsdale and H. J. Bhaba<sup>4</sup> wrote: