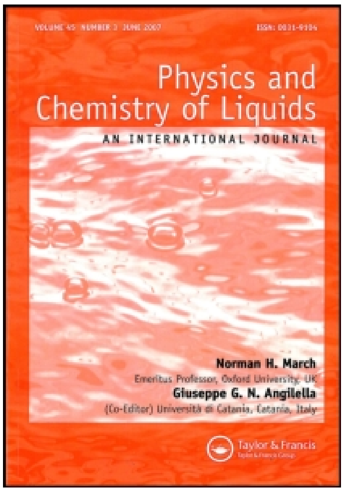

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Structure and forces in liquid metals: especially hydrogen

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Structure and Forces in Liquid Metals: Especially Hydrogen

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Motivated by the work of Corless and March on the interaction energy of an assembly of N protons in a high density electron gas, a systematic procedure based on the Born-Green-Yvon hierarchy is developed for deriving higher order correlation functions. In particular the three-body correlation function is altered from the Kirkwood form by multiplication by a factor $\exp(f)$, where f is expressed entirely in terms of the liquid structure factor $S(K)$.

The consequences of this approximation to the three-body correlations are investigated by working out the pressure dependence of the structure factor $S(K)$.

The theory provides a systematic iterative approach to derive a pair potential from measured structure data. In lowest order of the iteration, the results of Born-Green, Percus-Yevick and hypernetted chain theory are regained. In the next order however, these theories are transcended. We stress that the theory developed here is specific to liquid metals: the decoupling employed should not be used for insulating liquids.

1 INTRODUCTION

Much current interest in liquid metals centres round the relation between the electronic structure on the one hand and the ionic correlations on the other. Earlier work by Johnson and March[1,2] demonstrated that the ion-ion interaction potential in liquid metals had the general form to be expected from electron theory. But because of the lack of experimental structure data over a wide range of momentum transfer, plus the limitations of the approximate integral equations employed, progress in extracting the force laws has been slow.

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† The contribution of one of us (U. de A.) to this work was made during an extended visit to Imperial College.

Recently a study has been made by de Angelis and Forlani[3] of the structure of liquid metal hydrogen. This study, based essentially on a pair interaction of the form given by Corless and March,[4] has prompted us to go back to examine more carefully the implications of their work for the interaction energy of N protons in a high density electron gas.

We recognize, of course, that a proton, without any core electrons to weaken the conduction electron scattering, is a strong perturbation in a bath of electrons corresponding to normal liquid metal densities. But the interest in hydrogen is at very high pressures; for example the cold solid only becomes metallic at a pressure of the order of 1 megabar.

As we shall discuss below, our interest in liquid metal hydrogen has led us to a systematic procedure for discussing both pair and higher order correlation functions in simple liquid metals.

2 PAIR FUNCTION FOR HYDROGEN PLASMA

We note first that for a fixed proton configuration $\{\mathbf{R}\} \equiv \{\mathbf{R}_1, \ldots, \mathbf{R}_N\}$, solution of the Schrödinger equation would give the total interaction energy E $(\{\mathbf{R}\})$ for the protons, within the framework of the Born–Oppenheimer approximation. From this the canonical pair function $g(\mathbf{R}_1\mathbf{R}_2) = g(R_{12})$ is to be obtained in the usual way as

$$g(R_{12}) = \frac{V^2 \int \cdots \int e^{-\beta E(\{\mathbf{R}\})}\, d\mathbf{R}_3, \ldots, d\mathbf{R}_N}{\int \cdots \int e^{-\beta E(\{\mathbf{R}\})}\, d\mathbf{R}_1, \ldots, d\mathbf{R}_N} \, (N \to \infty) \qquad (2.1)$$

where V is the volume of the liquid.

The linear theory of Corless and March[4,5] yields the electron density $\rho(\mathbf{r}\{\mathbf{R}\})$ as a superposition of screened ion densities σ:

$$\rho(\mathbf{r}\{\mathbf{R}\}) = \sum_i \sigma(\mathbf{r} - \mathbf{R}_i) \qquad (2.2)$$

where σ depends only on the electron density in the Fermi bath i.e. it is a property of the screening of one proton in the electron assembly, and independent of local environment.

More generally, a form like Eq. (2.2) seems very plausible for, say, liquid metal Li. For Perrin, Taylor and March[6] have shown that a Korringa–Kohn–Rostoker band calculation leads to a form (2.2), the Li^+ ions admittedly being on a lattice, with σ correctly generated from a *single* Li^+ ion screened by the Fermi gas, the latter having been discussed by Dagens, Rasolt and Taylor.[7]

Thus the form (2.2) will be taken as the zeroth order starting point of the present theory.

2.1 Electrostatic potential

In the model based on Eq. (2.2), the total electrostatic potential at $\mathbf{r}$ is evidently given by

$$\Phi(\mathbf{r}, \{\mathbf{R}\}) = \sum_i \frac{e}{|\mathbf{r} - \mathbf{R}_i|} + \text{potential of } \rho(\mathbf{r})$$
$$= \sum_i \phi_s(\mathbf{r} - \mathbf{R}_i) \tag{2.3}$$

where $\phi_s(\mathbf{r})$ is the screened potential round one ion.

For a proton sitting at $\mathbf{R}_1$, we get the potential acting on it by taking the limit $\mathbf{r} \to \mathbf{R}_1$, but removing as usual the (infinite) potential of the proton's own charge. Then the result is found to be

$$\Phi(\mathbf{R}_1, \ldots, \mathbf{R}_N) = \sum_{i \neq 1} \phi_s(\mathbf{R}_1 - \mathbf{R}_i) + e \int \frac{\sigma(\mathbf{r}' - \mathbf{R}_1)}{|\mathbf{r}' - \mathbf{R}_1|} d\mathbf{r}'$$
$$= \sum_{i \neq 1} \phi_s(\mathbf{R}_1 - \mathbf{R}_i) + f(\mathbf{R}_1). \tag{2.4}$$

2.2 Force on proton at $\mathbf{R}_1$

According to the Hellmann–Feynman theorem, the force on a proton is given by the electric field in which the proton finds itself, times the (unit) charge of the proton. Hence the force acting on a proton at $\mathbf{R}_1$ when the remaining protons are at $\mathbf{R}_2, \ldots, \mathbf{R}_N$ is evidently given by

$$\mathbf{F}_1 = -\frac{\partial}{\partial \mathbf{R}_1} \Phi(\mathbf{R}_1, \ldots, \mathbf{R}_N). \tag{2.5}$$

But we also have, in terms of the energy of interaction E that

$$\mathbf{F}_1 = -\frac{\partial}{\partial \mathbf{R}_1} E(\mathbf{R}_1, \ldots, \mathbf{R}_N) \tag{2.6}$$

Thus we can write

$$E(\mathbf{R}_1, \ldots, \mathbf{R}_N) = \Phi(\mathbf{R}_1, \ldots, \mathbf{R}_N) + F(\mathbf{R}_2, \ldots, \mathbf{R}_N) \tag{2.7}$$

with F some as yet unknown function of the $N - 1$ variables shown.

2.3 n-particle correlation functions

The n-particle correlation function can be written in terms of a potential of mean force W_n as[8]

$$g_n(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \exp\{-\beta W_n(\mathbf{R}_1, \ldots, \mathbf{R}_n)\} \tag{2.8}$$

where W_n is defined as:

$$\nabla_1 W_n(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \frac{\int \cdots \int e^{-\beta E(\{\mathbf{R}\})} \nabla_1 E(\{\mathbf{R}\}) \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N}{\int \cdots \int e^{-\beta E(\{\mathbf{R}\})} \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N}$$

$$= -\frac{1}{\beta} \nabla_1 \ln \int \cdots \int e^{-\beta E(\{\mathbf{R}\})} \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N \quad (2.9)$$

Integrating this equation we evidently obtain

$$\beta W_n(\mathbf{R}_1 \cdots \mathbf{R}_n) = -\ln \int \cdots \int e^{-\beta E(\{\mathbf{R}\})} \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N$$

$$+ G(\mathbf{R}_2, \ldots, \mathbf{R}_n) \quad (2.10)$$

where G is the 'constant' of the $\mathbf{R}_1$ integration. Using eq. (2.7) we find

$$\beta W_n(\mathbf{R}_1, \ldots, \mathbf{R}_n) = -\ln \int \cdots \int e^{-\beta \Phi(\{\mathbf{R}\})} e^{-\beta F(\mathbf{R}_2, \ldots, \mathbf{R}_N)} \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N$$

$$+ G(\mathbf{R}_2, \ldots \mathbf{R}_n). \quad (2.11)$$

Substituting from eq. (2.4) into (2.11) we find

$$\beta W_n(\mathbf{R}_1 \cdots \mathbf{R}_n) = \beta f(\mathbf{R}_1) - \ln \int \cdots \int \exp\left[-\beta \sum_{i \neq 1} \phi_s(\mathbf{R}_1 - \mathbf{R}_i)\right]$$

$$\times \exp[-\beta F(\mathbf{R}_2, \ldots, \mathbf{R}_N)] \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N$$

$$+ G(\mathbf{R}_2, \ldots, \mathbf{R}_n) \quad (2.12)$$

which is readily rewritten as

$$\beta W_n(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \beta f(\mathbf{R}_1) + \beta \sum_{i=1}^{n} \phi_s(\mathbf{R}_{1i})$$

$$-\ln \int \cdots \int \prod_{i=n+1}^{N} e^{-\beta \phi_s(\mathbf{R}_1 - \mathbf{R}_i)} e^{-\beta F} \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N + G.$$

$$(2.13)$$

In particular

$$\beta W(R_{12}) = \beta \phi_s(R_{12}) + \beta f(R_1) + \text{function}(\mathbf{R}_1, \mathbf{R}_2) + G(\mathbf{R}_2). \quad (2.14)$$

Repeating the entire argument for the proton at R_2 we obtain

$$\beta W(R_{12}) = \beta \phi_s(R_{12}) + \beta f(R_2) + \text{function}(\mathbf{R}_2, \mathbf{R}_1) + G(\mathbf{R}_1). \quad (2.15)$$

For a fluid, the pair correlation function depends only on R_{12} and therefore

$$\begin{aligned}&\beta f(\mathbf{R}_1) + \text{function}(\mathbf{R}_1, \mathbf{R}_2) + G(R_2)\\ &\quad = \beta f(R_2) + \text{function}(\mathbf{R}_2, \mathbf{R}_1) + G(R_1) \equiv A(R_{12}) \qquad (2.16)\end{aligned}$$

and thus from eqs. (2.16), (2.15) and (2.9) we can write

$$g(R_{12}) = e^{-\beta\phi_s(R_{12})}e^{-A(R_{12})}. \qquad (2.17)$$

While, however, in principle, the above argument will allow the calculation of A from

a) The localized density $\sigma(r)$
b) The screened potential ϕ_s

in practice this does not seem presently feasible. Thus, we use eq. (2.17), plus the work of Johnson and March,[1,2] to motivate the calculation of A by making the zeroth order approximation

$$W(R_{12}) \simeq \phi_s(R_{12}) \qquad (2.18)$$

$$g(R_{12}) \simeq e^{-\beta\phi_s(R_{12})} \qquad (2.19)$$

A direct generalization to $n = 3$ evidently yields, in zeroth order

$$W(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = \phi_s(R_{12}) + \phi_s(R_{13}) + \phi_s(R_{23}) \qquad (2.20)$$

and hence the three-particle correlation function takes the Kirkwood form

$$g^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = g(R_{12})g(R_{13})g(R_{23}) \qquad (2.21)$$

Having thus motivated the zeroth order results (2.18) and (2.21) by appeal to the model of screened ions plus the work of Johnson and March,[1,2] the rest of the paper now makes use of the usual Born–Green–Yvon (BGY) hierarchy[8] to determine systematically the corrections to these zeroth order results. We start out from the exact relation between $g(R_{12})$, $g^{(3)}(R_1, R_2, R_3)$ and the pair potential $\phi(r)$; the so-called force equation.

Though the present approach has been motivated by considering liquid metal hydrogen, the iterative procedure developed below is proposed as a theory of structure for simple liquid metals.

3 FORCE EQUATION AND PAIR POTENTIAL FROM STRUCTURE DATA

The force equation reads

$$\frac{\partial W(R_{12})}{\partial \mathbf{R}_1} = \frac{\partial\phi(R_{12})}{\partial \mathbf{R}_1} + \rho_0 \int \frac{g^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)}{g(R_{12})} \frac{\partial\phi(R_{13})}{\partial \mathbf{R}_1}\, d\mathbf{R}_3 \qquad (3.1)$$

where ρ_0 is the number density N/V. If we insert the Kirkwood approximation (2.21) into eq. (3.1), then we obtain

$$\frac{\partial W(R_{12})}{\partial \mathbf{R}_1} \doteq \frac{\partial \phi(R_{12})}{\partial \mathbf{R}_1} + \rho_0 \int g(R_{13}) g(R_{23}) \frac{\partial \phi(R_{13})}{\partial \mathbf{R}_1} \, d\mathbf{R}_3 \tag{3.2}$$

This equation is equivalent to the Born–Green approximation in liquid structure theory if used as it stands. However, since from eq. (2.18) $\phi = \mathrm{W}$ in zeroth order, we can determine an improved pair potential from measured structure data by rewriting eq. (3.2) as

$$\frac{\partial \phi(R_{12})}{\partial \mathbf{R}_1} \doteq \frac{\partial W(R_{12})}{\partial \mathbf{R}_1} - k_B T \rho_0 \int \frac{\partial}{\partial \mathbf{R}_1} [g(R_{13}) - 1] g(R_{23}) d\mathbf{R}_3 \tag{3.3}$$

since $g(R_{13}) = \exp(-\beta W(R_{13}))$. Introducing the structure factor $S(K)$ through

$$S(K) = 1 + \rho_0 \int [g(r) - 1] \exp(i\mathbf{K} \cdot \mathbf{r}) d\mathbf{r} \tag{3.4}$$

eq. (3.3) yields the first-order result for the pair potential $\phi(R_{12})$:

$$\phi(R_{12}) = W(R_{12}) + \frac{k_B T}{8\pi^3 \rho_0} \int [S(K) - 1]^2 e^{i\mathbf{K} \cdot \mathbf{R}_{12}} \, d\mathbf{K} \tag{3.5}$$

It is of interest to note that, in the same spirit as the zeroth order model neglects the three-body term in the force equation, in the defining equation for the direct correlation function $c(r)$, namely

$$g(r) - 1 = h(r) = c(r) + \rho_0 \int h(\mathbf{r}') c(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' \tag{3.6}$$

we can take the zeroth order approximation as $h \doteq c$. Then replacing c by h in the integral term in the next approximation and treating $h - c$ as small leads back to Eq. (3.4) from both the Percus–Yevick and the hypernetted chain equations.

4 IMPROVED FORM OF THREE-PARTICLE CORRELATION FUNCTION

Clearly, if we inserted Eq. (3.5) back into the integral Eq. (3.1), we should be solving the Born–Green equation by the iterative method which was used by Johnson and March.[1] But to proceed systematically, we must consistently refine $g(R_{12}, R_{23}, R_{31})$ as well as ϕ and this we can do by means of the next member of the BGY hierarchy.

However, it will be helpful at this stage to consider the more general decoupling that we propose here for liquid metals. To do this, we introduce the unsymmetrical correlation function $g^{[n]}$ defined by Hill[8] as

$$g^{[n]}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \frac{V \int \cdots \int e^{-\beta E}\, \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N}{\int \cdots \int e^{-\beta E}\, \mathrm{d}\mathbf{R}_n, \ldots, \mathrm{d}\mathbf{R}_N} \tag{4.1}$$

Then a general result for fluids[8] is that

$$g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = g^{(n-1)}(\mathbf{R}_1, \ldots, \mathbf{R}_{n-1}) g^{[n]}(\mathbf{R}_1, \ldots, \mathbf{R}_n) \tag{4.2}$$

The unsymmetrical distribution functions enter the hierarchy through

$$\begin{aligned} &-k_B T \nabla_1 \ln g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) \\ &\quad = \sum_{i=2}^{n} \nabla_1 \phi_s(R_{1i}) + \rho_0 \int \nabla_1 \phi(R_{1,n+1}) g^{[n+1]}(\mathbf{R}_1, \ldots, \mathbf{R}_{n+1}) \mathrm{d}\mathbf{R}_{n+1}. \end{aligned} \tag{4.3}$$

Therefore the problem is to decouple the unsymmetrical correlation function $g^{[n]}(\mathbf{R}_1, \ldots, \mathbf{R}_n)$.

From Eq. (4.2) we have

$$g^{[n]}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \frac{V \int \cdots \int e^{-\beta \Phi(\{\mathbf{R}\})}\, \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N}{\int \cdots \int e^{-\beta \Phi(\{\mathbf{R}\})}\, \mathrm{d}\mathbf{R}_n, \ldots, \mathrm{d}\mathbf{R}_N} \tag{4.4}$$

and since we are taking the ion at $\mathbf{R}_n$ as the unsymmetrical one then we must take

$$\Phi(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \sum_{i \neq n} \phi_s(\mathbf{R}_n - \mathbf{R}_i) + f(\mathbf{R}_n) \tag{4.5}$$

with

$$f(\mathbf{R}_n) = e \int \frac{\sigma(\mathbf{R}_n - \mathbf{r})}{|\mathbf{R}_n - \mathbf{r}|}\, \mathrm{d}\mathbf{r}. \tag{4.6}$$

Then we get for $g^{[n]}$ the result

$$g^{[n]}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \frac{\begin{aligned} &V e^{-\beta f(\mathbf{R}_n)} e^{-\beta \phi_s(\mathbf{R}_{n,1})}, \ldots, e^{-\beta \phi_s(\mathbf{R}_{n,n-1})} \\ &\qquad \times \int \cdots \int \textstyle\prod_{i=n+1}^{N} e^{-\beta \phi_s(\mathbf{R}_{n,i})}\, \mathrm{d}\mathbf{R}_{n-1}, \ldots, \mathrm{d}\mathbf{R}_N \end{aligned}}{\begin{aligned} &\int e^{-\beta f(\mathbf{R}_n)} e^{-\beta \phi_s(\mathbf{R}_{n,1})}, \ldots, e^{-\beta \phi_s(\mathbf{R}_{n,n-1})}\, \mathrm{d}\mathbf{R}_n \\ &\qquad \times \int \cdots \int \textstyle\prod_{i=n-1}^{N} e^{-\beta \phi_s(\mathbf{R}_{n,i})}\, \mathrm{d}\mathbf{R}_{n+1}, \ldots, \mathrm{d}\mathbf{R}_N \end{aligned}} \tag{4.7}$$

which clearly satisfies the normalization condition. Apart from normalization coefficients we therefore take

$$g^{[n]}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = e^{-\beta \phi_s(\mathbf{R}_{n,1})} e^{-\beta \phi_s(\mathbf{R}_{n,2})}, \ldots, e^{-\beta \phi_s(\mathbf{R}_{n,n-1})} \tag{4.8}$$

The consequences of all this for the decoupling of the hierarchy for the symmetrical n-particle correlation function $g^{(n)}$ is discussed in the Appendix.

Here our immediate aim is to get the next order approximation for $g^{(3)}$ from the hierarchy and we do this by inserting the lowest order decoupling for $g^{(4)}$ in Eq. (4.3). Thus we get

$$-k_B T\nabla_1 \ln g^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = \nabla_1[\phi_s(R_{12}) + \phi_s(R_{13})] + \rho_0 \int \nabla_1 \phi_s(R_{14}) e^{-\beta\phi_s(R_{41})} e^{-\beta\phi_s(R_{42})} e^{-\beta\phi_s(R_{43})}\, d\mathbf{R}_4. \tag{4.9}$$

To lowest order, we can replace each $\phi_s(R_{ij})$ in the integral by $W(R_{ij})$ and then $g(R_{14})\nabla_1 W(R_{14}) = -(1/\beta)\nabla_1(g(R_{14}) - 1)$ so we have

$$-k_B T\nabla_1 \ln g^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = \nabla_1[\phi_s(R_{12}) + \phi_s(R_{13})] - k_B T\rho_0 \nabla_1 \int h(R_{14}) g(R_{24}) g(R_{34})\, d\mathbf{R}_4 \tag{4.10}$$

that is

$$\ln g^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = -\beta\phi_s(R_{12}) - \beta\phi_s(R_{13}) - \beta\phi_s(R_{23}) + \rho_0 \int h(R_{14}) g(R_{24}) g(R_{34})\, d\mathbf{R}_4 \tag{4.11}$$

where $\phi_s(R_{23})$ has been added as a "constant" of integration for obvious symmetry reasons. For $\phi_s(R_{ij})$ in Eq. (4.12) we must now use the first order result for the pair potential, namely Eq. (3.4), which we write as

$$\beta\phi(R_{ij}) = \beta W(R_{ij}) + \Delta\phi(R_{ij}) \tag{4.12}$$

with

$$\Delta\phi(R_{ij}) = \frac{1}{8\pi^3\rho_0} \int [S(K) - 1]^2 e^{i\mathbf{K}\cdot\mathbf{R}_{ij}}\, d\mathbf{K}. \tag{4.13}$$

Then we obtain

$$g^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = g(R_{12}) g(R_{13}) g(R_{23}) \exp(-\Delta\phi(R_{12}) \exp(-\Delta\phi(R_{13})) \times \exp(-\Delta\phi(R_{23}) \exp\left\{\rho_0 \int h(R_{14}) g(R_{24}) g(R_{34})\, d\mathbf{R}_4\right\} \tag{4.14}$$

This can be put into a somewhat simpler form if we do not insert the term -1 in $g(R_{14})$ in Eq. (4.11): in fact in this case the last exponential term in $g^{(3)}$ is the product of three g's, which we can express in terms of the total correlation function h as

$$\begin{aligned}\int g(R_{14})g(R_{24})g(R_{34})\mathrm{d}\mathbf{R}_4 &= \int h(R_{14})h(R_{24})h(R_{34})\mathrm{d}\mathbf{R}_4 \\ &+ \int h(R_{14})h(R_{24})\mathrm{d}\mathbf{R}_4 + \int h(R_{14})h(R_{34})\mathrm{d}\mathbf{R}_4 \\ &+ \int h(R_{24})h(R_{34})\mathrm{d}\mathbf{R}_4. \qquad (4.15)\end{aligned}$$

Here we have dropped all the terms not involving R_{12}, R_{13}, R_{23} as they have to cancel to give the correct asymptotic behaviour of $g^{(3)}(R_{12}, R_{13}, R_{23})$. The last three terms in Eq. (4.16) give $\Delta\phi(R_{12})$, $\Delta\phi(R_{13})$, $\Delta\phi(R_{23})$ respectively and the first term can also be written in terms of structure factors as

$$\begin{aligned}\rho_0 \int g(R_{14})g(R_{24})g(R_{34})\mathrm{d}\mathbf{R}_4 &= f(\mathbf{R}_{13}, \mathbf{R}_{23}) + \Delta\phi(R_{12}) + \Delta\phi(R_{13}) \\ &+ \Delta\phi(R_{23}) \qquad (4.16)\end{aligned}$$

with

$$\begin{aligned}f(\mathbf{R}_{13}, \mathbf{R}_{23}) = \frac{1}{(8\pi^3\rho_0)^2} &\iint \mathrm{d}\mathbf{K}\, \mathrm{d}\mathbf{K}'[S(K) - 1][S(K') - 1] \\ &\times [S(|\mathbf{K} + \mathbf{K}'|) - 1]e^{-i\mathbf{K}\cdot\mathbf{R}_{13}}e^{-i\mathbf{K}'\cdot\mathbf{R}_{23}} \qquad (4.17)\end{aligned}$$

Of course, f can be written in terms of any two of the vectors $\mathbf{R}_{12}$, $\mathbf{R}_{13}$, $\mathbf{R}_{23}$, say $\mathbf{R}$, $\mathbf{R}'$. Equation (4.17) can be obtained for $n = 3$ from the general expression (A.8) in the Appendix but we have preferred to derive it directly here. Thus the $\Delta\phi$ in Eq. (4.14) cancel and we are left with a basic result for the 3-particle correlation function in liquid metals

$$g^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = g(R_{12})g(R_{13})g(R_{23})\exp[f(\mathbf{R}, \mathbf{R}')]. \qquad (4.18)$$

4.1 Second-order correction to pair potential from structure data

Our primary objective is to pursue consistently the second order theory for the pair potential, from measured structure data. To do so we write

$$g^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = g_K^{(3)} + \Delta \qquad (4.19)$$

where $g_K^{(3)}$ is the Kirkwood result (2.21). Then we find from Eq. (4.18)

$$\Delta = g_K^{(3)}[e^{f(\mathbf{R},\mathbf{R}')} - 1]. \qquad (4.20)$$

Evidently we must now insert the first-order results for both ϕ and $g^{(3)}$ in the force equation, when we find

$$\begin{aligned}\nabla_1\phi(R_{12}) = \nabla_1 W(R_{12}) &- \rho_0\int g(R_{23})g(R_{31})\nabla_1 W(R_{13})\mathrm{d}R_3\\ &- \rho_0 k_B T\int g(R_{23})g(R_{31})\nabla_1\Delta\phi(R_{13})\mathrm{d}\mathbf{R}_3\\ &+ \rho_0\int g(R_{23})g(R_{31})[e^{f(\mathbf{RR}')} - 1]\nabla_1 W(R_{13})\mathrm{d}\mathbf{R}_3.\end{aligned} \tag{4.21}$$

Using the identity

$$g(R_{13})\nabla_1 W(R_{13}) = -\frac{1}{\beta}\nabla_1 h(R_{13}) \tag{4.22}$$

we have

$$\begin{aligned}\nabla_1\phi(R_{12}) = \nabla_1\left[W(R_{12}) + \rho_0 k_B T\int h(R_{13})g(R_{23})\mathrm{d}\mathbf{R}_3\right]&\\ - \rho_0 k_B T\int g(R_{23})g(R_{13})\nabla_1\Delta\phi(R_{13})\mathrm{d}\mathbf{R}_3&\\ - \rho_0 k_B T\int g(R_{23})[e^{f(\mathbf{RR}')} - 1]\nabla_1 h(R_{13})\mathrm{d}R_3.&\end{aligned} \tag{4.23}$$

This can be conveniently rewritten as

$$\begin{aligned}\nabla_1\phi(R_{12}) = \nabla_1\Big\{W(R_{12}) &+ k_B T\Delta\phi(R_{12})\\ &- \rho_0 k_B T\int h(R_{13})g(R_{23})[e^{f(\mathbf{RR}')} - 1]\mathrm{d}\mathbf{R}_3\Big\}\\ &+ \rho_0 k_B T\int h(R_{13})g(R_{23})e^{f(\mathbf{RR}')}\nabla_1 f(\mathbf{RR}')\mathrm{d}\mathbf{R}_3\\ &- \rho_0 k_B T\int g(R_{23})g(R_{31})\nabla_1\Delta\phi(R_{13})\mathrm{d}\mathbf{R}_3.\end{aligned} \tag{4.24}$$

Equation (4.24) represents a consistent second-order theory for the pair interaction $\phi(R_{12})$ in terms of measured structural data. If we now argue that f and $\Delta\phi$ are slowly varying functions of $\mathbf{R}_1$, which may be reasonable when we remember they were both zero in lowest order, and furthermore that f is small enough to allow the expansion of the exponential in lowest order only, then we can set to zero the last two terms. In this approximation, we can carry out the integration immediately to obtain the approximate result

$$\phi(R_{12}) = W(R_{12}) + k_B T \Delta\phi(R_{12}) - \rho_0 k_B T \int h(R_{13}) g(R_{23}) f(\mathbf{R}_{13}, \mathbf{R}_{23}) \mathrm{d}\mathbf{R}_3 \tag{4.25}$$

for the second order correction to the pair potential. Now $\Delta\phi$ is already written in Eq. (3.5) in terms of the measured structure factor. If we use convolution properties to rewrite the last term in Eq. (4.25) in terms of structure factors we obtain

$$\begin{aligned}\phi(R_{12}) = W(R_{12}) &+ \frac{k_B T}{8\pi^3 \rho_0} \int [S(K) - 1]^2 e^{i\mathbf{K}\cdot\mathbf{R}_{12}} \mathrm{d}\mathbf{K} \\ &- \frac{k_B T}{(8\pi^3 \rho_0)^2} \iint \mathrm{d}\mathbf{K}\, \mathrm{d}\mathbf{K}' [S(K) - 1][S(K') - 1] \\ &\times S(|\mathbf{K} + \mathbf{K}'|) - 1]^2 e^{i\mathbf{K}'\cdot\mathbf{R}_{12}} \\ &- \frac{k_B T}{(8\pi^3 \rho_0)^3} \iint \mathrm{d}\mathbf{K}\, \mathrm{d}\mathbf{K}'\, \mathrm{d}\mathbf{K}'' [S(K) - 1][S(K') - 1] \\ &\times [S(|\mathbf{K} + \mathbf{K}'|) - 1][S(K'') - 1] \\ &\times [S(|\mathbf{K} + \mathbf{K}' + \mathbf{K}''|) - 1] e^{i\mathbf{K}'\cdot\mathbf{R}_{12}}\end{aligned} \tag{4.26}$$

Thus the main result of this argument is Eq. (4.18) for the three-body correlation function, given the measured pair function. An important consequence of this form of $g^{(3)}$ is the result (4.24) for the second-order pair potential. The further approximation to this potential embodied in Eq. (4.26) is valid if the slowly varying assumptions made in going from Eq. (4.24) to (4.25), plus the requirement that f is small, are appropriate. In general, these assumptions should be checked by solving Eq. (4.24).

5 PRESSURE DEPENDENCE OF STRUCTURE FACTOR: A TEST OF $g^{(3)}$

Whereas pair correlation functions can be obtained to a degree of accuracy from scattering experiments, there is no similar practical approach as yet for measuring the triplet function $g^{(3)}$ essentially because the cross-sections for scattering of radiation are so small.

It has been shown however[9,10] that $g^{(3)}$ can be related to the isothermal pressure derivative of the structure factor, which is a measurable quantity.

In particular, by focussing on the difference between $g^{(3)}$ and the superposition value, namely

$$H(\mathbf{r}, \mathbf{s}) = g^{(3)}(\mathbf{r}, \mathbf{s}) - g(r)g(s)g(t) \tag{5.1}$$

Egelstaff *et al.*[10] could show that the quantity

$$\bar{H}(Q) = \rho_0^2 \int e^{-i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r} \int H(\mathbf{r}, \mathbf{s}) d\mathbf{s} \tag{5.2}$$

is directly related to the isothermal pressure derivative of $S(Q)$ and other measurable quantities involving $S(Q)$, including its long wavelength limit which is, essentially, the isothermal compressibility. We wish here to invert the problem: by considering $\bar{H}(Q)$ as a known experimental quantity we examine the prediction of the present theory of $g^{(3)}$ in section 4 above.

We shall work only to first order in f in the exponential in our basic result (4.18). Then we can write

$$g^{(3)} = g_K^{(3)} + g_K^{(3)} f(\mathbf{R}, \mathbf{R}') = g_K^{(3)} - H(\mathbf{R}, \mathbf{R}') \tag{5.3}$$

where

$$g_K^{(3)} = g(R_{12})g(R_{13})g(R_{23})$$

is the zeroth order result.

For notational convenience we write

$$T(K) = S(K) - 1$$

$$T(\mathbf{K}, \mathbf{K}') = \frac{1}{(8\pi^3\rho_0)^2} [S(K') - 1][S(|\mathbf{K} + \mathbf{K}'|) - 1]. \tag{5.4}$$

Then we have:

$$H(\mathbf{R}_{12}, \mathbf{R}_{13}) = -g_K^{(3)} \iint d\mathbf{K}\, d\mathbf{K}' T(K) T(\mathbf{K}, \mathbf{K}') e^{-i\mathbf{K}\cdot\mathbf{R}_{12}} e^{-i\mathbf{K}'\cdot\mathbf{R}_{13}} \tag{5.5}$$

If we now set

$$\mathbf{R}_1 - \mathbf{R}_2 = \mathbf{s}, \mathbf{R}_1 - \mathbf{R}_3 = \mathbf{r}, \mathbf{R}_2 - \mathbf{R}_3 = \mathbf{t}$$

we find

$$H(\mathbf{r}, \mathbf{s}) = -g(r)g(s)g(t) \iint d\mathbf{K}\, d\mathbf{K}' T(K) T(\mathbf{K}, \mathbf{K}') e^{-i\mathbf{K}\cdot\mathbf{s}} e^{-i\mathbf{K}'\cdot\mathbf{r}}. \tag{5.6}$$

Defining $\bar{H}(r)$ by

$$\bar{H}(r) = \rho_0 \int H(\mathbf{r}, \mathbf{s}) d\mathbf{s}$$

we obtain the result

$$\begin{aligned}\bar{H}(r) = {} & -\rho_0 g(r) \iint d\mathbf{K}\, d\mathbf{K}' T(K) T(\mathbf{K}, \mathbf{K}') e^{-i\mathbf{K}'\cdot\mathbf{r}} \\ & \times \int g(s) g(|\mathbf{r}-\mathbf{s}|) e^{-i\mathbf{K}\cdot\mathbf{s}}\, d\mathbf{s} \end{aligned} \tag{5.7}$$

The last integral can be written as

$$\int h(s) h(|\mathbf{r}-\mathbf{s}|) e^{-i\mathbf{K}\cdot\mathbf{s}}\, d\mathbf{s} + \int h(s) e^{-i\mathbf{K}\cdot\mathbf{s}}\, d\mathbf{s} + \int h(|\mathbf{r}-\mathbf{s}|) e^{-i\mathbf{K}\cdot\mathbf{s}}\, d\mathbf{s}$$

which, introducing the Fourier transform $\tilde{h}(K) = \int h(r) e^{i\mathbf{K}\cdot\mathbf{r}}\, d\mathbf{r}$, of the total correlation function h, becomes

$$\frac{1}{8\pi^3} \int d\mathbf{q}\, \tilde{h}(q) \tilde{h}(|\mathbf{q}+\mathbf{K}|) e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}} + \tilde{h}(K) + e^{-i\mathbf{K}\cdot\mathbf{r}} \tilde{h}(K)$$

Using the relation (3.3) between $\tilde{h}(K)$ and $S(K)$, Eq. (5.7) takes the form

$$\begin{aligned}\bar{H}(\mathbf{r}) = {} & -8\pi^3 \rho_0 g(r) \iint d\mathbf{K}\, d\mathbf{K}'\, d\mathbf{q}\, T(K) T(\mathbf{K}, \mathbf{K}') T(\mathbf{K}, \mathbf{q}) e^{-i(\mathbf{K}'+\mathbf{q})\cdot\mathbf{r}} e^{-i\mathbf{K}\cdot\mathbf{r}} \\ & - g(r) \iint d\mathbf{K}\, d\mathbf{K}' T^2(K) T(\mathbf{K}, \mathbf{K}') e^{-i\mathbf{K}'\cdot\mathbf{r}} \\ & - g(r) \iint d\mathbf{K}\, d\mathbf{K}' T^2(K) T(\mathbf{K}, \mathbf{K}') e^{-i(\mathbf{K}'+\mathbf{K})\cdot\mathbf{r}} \end{aligned} \tag{5.8}$$

Now we calculate the quantity

$$\bar{H}(Q) = \rho_0 \int \bar{H}(\mathbf{r}) e^{-i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r}$$

to obtain

$$\begin{aligned}\bar{H}(Q) = {} & -8\pi^3 \rho_0^2 \iiint d\mathbf{K}\, d\mathbf{K}'\, d\mathbf{q}\, T(K) T(\mathbf{K}, \mathbf{K}') T(\mathbf{K}, \mathbf{q}) \\ & \times \int g(r) e^{-i(\mathbf{K}+\mathbf{K}'+\mathbf{q}-\mathbf{Q})\cdot\mathbf{r}}\, d\mathbf{r} - \rho_0 \iint d\mathbf{K}\, d\mathbf{K}' T^2(K) T(\mathbf{K}, \mathbf{K}') \\ & \times \int g(r) e^{-i(\mathbf{K}'-\mathbf{Q})\cdot\mathbf{r}}\, d\mathbf{r} - \rho_0 \iint d\mathbf{K}\, d\mathbf{K}'\, T^2(K) T(\mathbf{K}, \mathbf{K}') \\ & \times \int g(r) e^{-i(\mathbf{K}'-\mathbf{Q}+\mathbf{K})\cdot\mathbf{r}}\, d\mathbf{r}. \end{aligned} \tag{5.9}$$

Since the integrals involving the pair function are

$$\int g(r)e^{-i\mathbf{P}\cdot\mathbf{r}}\,d\mathbf{r} = \tilde{h}(P) + (2\pi)^3\delta(\mathbf{P})$$

the final result for $\bar{H}(Q)$ can be expressed in terms of structure factors alone as

$$\begin{aligned}\bar{H}(Q) = &-\frac{1}{8\pi^3\rho_0}[S(Q) - 1]\int d\mathbf{K}[S(K) - 1]^2 \\ &\times \{[S(|\mathbf{Q} + \mathbf{K}| - 1] + [S(|\mathbf{Q} - \mathbf{K}|) - 1]\} \\ &-\frac{1}{(8\pi^3\rho_0)^2}\iint d\mathbf{K}\,d\mathbf{K}'G(\mathbf{K}, \mathbf{K}') \\ &\times [F_2(\mathbf{K}, \mathbf{K}', \mathbf{Q}) + F_1(\mathbf{K}, \mathbf{K}', \mathbf{Q})]\end{aligned} \tag{5.10}$$

where:

$$\begin{aligned}G(\mathbf{K}, \mathbf{K}') &= [S(K) - 1][S(K') - 1][S(|\mathbf{K} + \mathbf{K}'|) - 1] \\ F_1(\mathbf{K}, \mathbf{K}', \mathbf{Q}) &= \frac{1}{8\pi^3\rho_0}\int d\mathbf{q}[S(q) - 1][S(|\mathbf{K} + \mathbf{q}|) - 1] \\ &\quad\times [S(\mathbf{K} + \mathbf{K}' + \mathbf{q} - \mathbf{Q}) - 1] \\ F_2(\mathbf{K}, \mathbf{K}', \mathbf{Q}) &= [S(K) - 1]\{[S(|\mathbf{K} - \mathbf{Q}| - 1] + [S(|\mathbf{K} + \mathbf{K}' - \mathbf{Q}|) - 1]\} \\ &\quad + S(|\mathbf{Q} + \mathbf{K}'|) - 1][S(|\mathbf{Q} - \mathbf{K} - \mathbf{K}'|) - 1].\end{aligned} \tag{5.11}$$

These last two equations contain the prediction, in terms of measurable structure factors, for $\bar{H}(Q)$ from the theory of the triplet correlation function developed in this paper and it would be of considerable interest to test it in particular cases.

6 CONCLUDING REMARKS AND SUMMARY

It will have occurred to the reader familiar with density expansion methods in the theory of imperfect gases that there is a formal similarity to the theory developed here. But that is where the similarity ceases. This is because the effective interionic potentials in liquid metals are defined in terms of a Fermi bath of a given density, and by asking for the energy difference between two ions in the Fermi sea at distance R_{12} and at infinite distance. Secondly, it must be stressed that in all the iterative development, it is essential that the pair function is always written exactly, that is in terms of the potential of mean force W and not in terms of ϕ. Thus, the present philosophy is entirely the same as that adopted by Johnson and March.[1] While we have not, of course, been able to discuss convergence of our procedure, as it is obviously impossible at present to get a useful expression for the *n*th term in the iteration, we anticipate from earlier results on the approximate integral equations that there should be reasonable convergence, but this will have to be checked out in particular cases as they arise.

In summary, the main achievements of this paper are:

1) To obtain expressions in first order for the pair potential $\phi(r)$ and the triplet correlation function $g^{(3)}$ which are directly calculable from measured structure data on liquid metals.

2) To evaluate the second order correction to $\phi(r)$ approximately in terms of the measured structure factor.

3) To give a theory of the pressure dependence of the structure factor on the basis of the first-order theory of $g^{(3)}$. We stress again that this is the route to test the present theory of $g^{(3)}$ against an experimentally measurable quantity. Understanding the present measurements of Egelstaff *et al.*[10] on Rb is a simpler matter on our zeroth order and first order theories. If, as for high density hydrogen, we study the scaling with the Fermi wave number k_f, then their $\rho_0^{1/3} \propto k_f$ model, which they point out fits the pressure data, follows. This observation already supports the considerations of the present paper.

However, we caution finally that the procedure used in this paper must not be used for insulating liquids such as argon. One must ask about the nature and range of the forces first, and after that develop an appropriate decoupling. In other words, one should not expect one universal decoupling approximation to cover such widely different force laws as exist in liquid Al or Pb on the one hand, and liquid argon on the other.

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Appendix

The purpose of this Appendix is to give the decoupling of the *n*-body correlation function to lowest order, from the BGY hierarchy, for *liquid metals.* From Eqs. (4.6) and (4.10) we have

$$-k_B T\nabla_1 \ln g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \sum_{i=2}^{n} \nabla_1 \phi_s(R_{1i}) + \rho_0 \int \nabla_1 \phi_s(R_{1,n+1}) e^{-\beta\phi_s(R_{n+1,1})}, \ldots, e^{-\beta\phi_s(R_{n+1,n})}\, \mathrm{d}\mathbf{R}_{n+1}. \tag{A.1}$$

In the integral, we use the lowest order result

$$e^{-\beta_s(R_{n+1,1})}\nabla_1 \phi_s(R_{n+1,1}) = -\frac{1}{\beta}\nabla_1 g(R_{n+1,1}) \tag{A.2}$$

and then we find

$$-k_B T\nabla_1 \ln g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \sum_{i=2}^{n} \nabla_1 \phi_s(R_{1i}) - \rho_0 k_B T \nabla_1 \int g(R_{n+1,1}), \ldots, g(R_{n+1,n}) \mathrm{d}\mathbf{R}_{n+1}. \tag{A.3}$$

Integrating this equation yields

$$\ln g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = -\beta \sum_{i=2}^{n} \phi_s(R_{1i}) + \rho_0 \int g(R_{n+1,1}), \ldots, g(R_{n+1,n}) \mathrm{d}\mathbf{R}_n + f(\mathbf{R}_2, \ldots, \mathbf{R}_n). \tag{A.4}$$

Repeating the argument for all ∇_α, $\alpha = 2, 3, \ldots, n$, we conclude that the symmetrized result with the appropriate asymptotic behaviour is

$$\ln g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \sum_{i \neq j} \sum_{j} [-\beta\phi_s(R_{ij})] + \rho_0 \int g(R_{n+1,1}), \ldots, g(R_{n+1,n}) \mathrm{d}\mathbf{R}_{n+1}. \tag{A.5}$$

Having used zeroth order approximations in the integral we should use first order $\beta\phi_s = \beta W + \Delta\phi$ and then

$$g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \prod_{i \neq j} [g(R_{ij}) e^{-\Delta\phi(R_{ij})}] \times \exp\left\{\rho_0 \int g(R_{n+1,1}), \ldots, g(R_{n+1,n}) \mathrm{d}\mathbf{R}_n\right\}. \tag{A.6}$$

But now the integral in the exponential can be written in terms of total correlation functions; in doing so all the exponents of $\Delta\phi$ cancel, just as was demonstrated to be the case for $n = 3$ in section 4. The final result is given by

$$g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \prod_{i \neq j} g(R_{ij}) \exp\left\{\rho_0 \int h(R_{n+1,1}), \ldots, h(R_{n+1,n}) \mathrm{d}\mathbf{R}_{n+1}\right\}. \tag{A.7}$$

Using convolution properties, this can be written in terms of structure factors as

$$g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = \prod_{i \neq j} g(R_{ij}) \exp\{f(\mathbf{R}_{n1}, \mathbf{R}_{n2}, \ldots, \mathbf{R}_{n,n-1})\} \tag{A.8}$$

with

$$\begin{aligned} f(R_{n,1}, \ldots, R_{n,n-1}) = \frac{1}{(8\pi^3\rho_0)^{n-1}} \int \cdots \int & \mathrm{d}\mathbf{K}_1, \ldots, \mathrm{d}\mathbf{K}_{n-1} \\ & \times [S(K_1) - 1] \cdots [S(K_{n-1}) - 1] \\ & \times [S(|\mathbf{K}_1 + \mathbf{K}_2 + \cdots + \mathbf{K}_{n-1}|) - 1] \\ & \times e^{-i\mathbf{K}_1 \cdot \mathbf{R}_{n1}} e^{-i\mathbf{K}_2 \cdot \mathbf{R}_{n2}}, \ldots, e^{-i\mathbf{K}_{n-1} \cdot \mathbf{R}_{n,n-1}}. \end{aligned} \tag{A.9}$$

Equations (A.8) and (A.9) give the first-order results for the n-particle correlation function in a liquid metal in terms of measurable quantities, namely pair functions and structure factors.

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