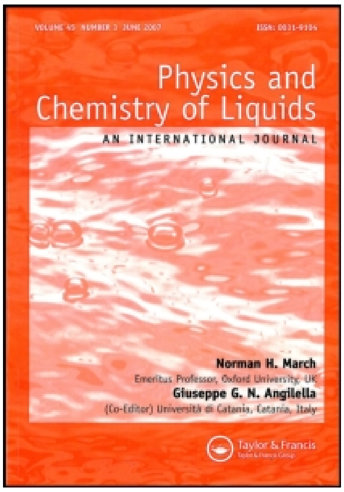

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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C. Amovilli[a]; N. H. March[bc]; Á. Nagy[d]
[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy [b] Department of Physics, University of Antwerp, Antwerpen, Belgium [c] Oxford University, Oxford, England [d] Department of Theoretical Physics, University of Debrecen, Debrecen, Hungary

To cite this Article Amovilli, C. , March, N. H. and Nagy, Á.(2009) 'Exact integral relation between the triplet correlation function in the ground state of the completely polarised homogeneous electron fluid and the pair function: comparison with the classical liquid argon result', Physics and Chemistry of Liquids, 47: 1, 5 — 8

To link to this Article: DOI: 10.1080/00319100802261069

URL: http://dx.doi.org/10.1080/00319100802261069

Physics and Chemistry of Liquids
Vol. 47, No. 1, February 2009, 5–8

Exact integral relation between the triplet correlation function in the ground state of the completely polarised homogeneous electron fluid and the pair function: comparison with the classical liquid argon result

C. Amovilli[a]*, N.H. March[bc] and Á. Nagy[d]

[a]*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy;* [b]*Department of Physics, University of Antwerp, Antwerpen, Belgium;* [c]*Oxford University, Oxford, England;* [d]*Department of Theoretical Physics, University of Debrecen, Debrecen, Hungary*

(*Received 9 June 2008; final version received 10 June 2008*)

In a classical monoatomic liquid such as argon, there is a well-known relation between an integral over the triplet correlation function and the pair function, independent of the interparticle interaction. Here, we make a start on establishing a quantum-mechanical analogue by considering the ground state of the completely spin-polarised homogeneous electron fluid. Again, an exact relation is then established, but now at $T=0$, for such a Fermion fluid, where only Pauli principle repulsions exist between all the electrons. A possible generalisation to embrace additional electron–electron Coulombic repulsions is thereby conjectured.

Keywords: triplet correlation function; pair density; uniform electron fluid

1. Introduction

In classical liquids such as argon, it has been known from studies going back, at very least, to the work of Schofield [1] (see also [2]), that there exists an exact integral relation between the important triplet correlation function $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ and the density dependence of the pair function $g(r)$ which is directly observably by neutron diffraction experiments.

Here, we make a modest start, via a simple example, of seeking a possible quantum-mechanical generalisation, but now at $T=0$, of such a classical relation between an integral over the triplet correlation function and the density dependence of the pair function.

The simple example referred to above has been taken as the completely spin-polarised (ferromagnetic) state of a homogeneous electron fluid (HEF) at $T=0$ in the high density limit. Then, interactions between all pairs of electrons are the same: namely the Pauli principle repulsions. We shall then obtain in Section 3 below an explicit relation for an integral over the triplet electronic correlation function, this being motivated by the classical statistical-mechanical relation referred to above. Quite explicitly [1,2], this reads, say for argon with n denoting the number density of atoms,

$$2g(r) + n\int\left[g^{(3)}(\mathbf{r}, \mathbf{R}) - g(r)\right]\mathrm{d}\mathbf{R} = S(0)\left[2g(r) + n\frac{\partial g}{\partial n}\right] \tag{1}$$

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*Corresponding author. Email: amovilli@dcci.unipi.it

ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319100802261069
http://www.informaworld.com

where $g(r)$ is the pair correlation function, $g^{(3)}$ the triplet analogue, and $\mathbf{R}=\mathbf{r}_3-\mathbf{r}_1$ and $\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1$ are used. $S(0)$ is the long-wavelength limit of the liquid structure factor, which is, in essence, the Fourier transform of $g(r)-1$ [3]. The limit $k\to 0$ of liquid structure factor $S(k)$ is well known from fluctuation theory to be given by

$$S(0) = nk_BT\mathcal{K}_T, \tag{2}$$

where $\mathcal{K}_T$ is the isothermal compressibility. We therefore seek below the quantum-mechanical analogue of the classical relation (1), but now at $T=0$, for the ferromagnetic electron fluid.

2. Three-electron density matrix

Following the early study of Cohen and Frishberg [4], who considered the hierarchical equations for reduced density matrices, we quote their Equation (3.4) which can be utilised for the HEF with spins parallel. Letting x denote at first both space and spin variables, they obtain the Hartree–Fock approximation appropriate to the HEF case:

$$\rho_3(x_1,x_2,x_3;x_1',x_2',x_3') = \frac{1}{3!}\begin{vmatrix} \rho_1(x_1;x_1') & \rho_1(x_1;x_2') & \rho_1(x_1;x_3') \\ \rho_1(x_2;x_1') & \rho_1(x_2;x_2') & \rho_1(x_2;x_3') \\ \rho_1(x_3;x_1') & \rho_1(x_3;x_2') & \rho_1(x_3;x_3') \end{vmatrix}, \tag{3}$$

ρ_3 and ρ_1 being third- and first-order density matrices. But in turn, the second-order matrix ρ_2 is written in terms of the first-order quantity ρ_1 in [4] as

$$\rho_2(x_1,x_2;x_1',x_2') = \frac{1}{2!}\begin{vmatrix} \rho_1(x_1;x_1') & \rho_1(x_1;x_2') \\ \rho_1(x_2;x_1') & \rho_1(x_2;x_2') \end{vmatrix} \tag{4}$$

Hence, by expanding the determinant for ρ_3, this three-electron property is immediately written in terms of ρ_1 and ρ_2. This we utilise below for the HEF.

3. Triplet electronic correlation function for a ferromagnetic HEF

Let us suppose that the electron density of the HEF is n. Then, if the Fermi momentum is denoted by p_f, since the volume of a cell in phase space which can hold two electrons with opposite spins is equal to h^3 we can write the relation between n and p_f for the spin-polarised HEF as

$$n = \frac{4\pi p_f^3}{3h^3}. \tag{5}$$

Then the desired first-order spinless density matrix $\gamma(\mathbf{r}_1;\mathbf{r}_2)$ in the ground state of the ferromagnetic phase is given by

$$\gamma(\mathbf{r}_1;\mathbf{r}_2) = \frac{1}{8\pi^3}\int_{k<k_f} \exp[i\mathbf{k}\cdot(\mathbf{r}_2-\mathbf{r}_1)]\mathrm{d}\mathbf{k}, \tag{6}$$

where k_f is the Fermi wave number given by $k_f = p_f/\hbar$. This then yields

$$\gamma(\mathbf{r}_1;\mathbf{r}_2) = \frac{3nj_1(k_f|\mathbf{r}_2-\mathbf{r}_1|)}{k_f|\mathbf{r}_2-\mathbf{r}_1|} \tag{7}$$

where $j_1(x)$ is the first-order spherical Bessel function $(\sin x - x\cos x)/x^2$. Using Equation (4), we obtain from $\Gamma_2(\mathbf{r}_1,\mathbf{r}_2)$, the diagonal element of the spinless second-order density matrix, the result that

$$\Gamma_2(\mathbf{r}_1,\mathbf{r}_2) = \frac{n^2}{2}\left\{1 - 9\left[\frac{j_1(k_f|\mathbf{r}_2-\mathbf{r}_1|)}{k_f|\mathbf{r}_2-\mathbf{r}_1|}\right]^2\right\}. \tag{8}$$

Utilising ρ_3 in Equation (3) we achieve the following result for the corresponding spinless three-particle density Γ_3:

$$\begin{aligned}\Gamma_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \frac{1}{6}\{&n^3 + 2\gamma(\mathbf{r}_1;\mathbf{r}_2)\gamma(\mathbf{r}_2;\mathbf{r}_3)\gamma(\mathbf{r}_3;\mathbf{r}_1)\\ &- n[\gamma(\mathbf{r}_1;\mathbf{r}_2)\gamma(\mathbf{r}_2;\mathbf{r}_1) + \gamma(\mathbf{r}_1;\mathbf{r}_3)\gamma(\mathbf{r}_3;\mathbf{r}_1) + \gamma(\mathbf{r}_2;\mathbf{r}_3)\gamma(\mathbf{r}_3;\mathbf{r}_2)]\}.\end{aligned} \tag{9}$$

Now, by recognising that

$$n^2 - \gamma(\mathbf{r}_1;\mathbf{r}_2)\gamma(\mathbf{r}_2;\mathbf{r}_1) = 2\Gamma_2(\mathbf{r}_1,\mathbf{r}_2) \tag{10}$$

and using idempotency of γ, the following integral is readily derived:

$$\int\left[\Gamma_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) - \frac{n}{3}\Gamma_2(\mathbf{r}_1,\mathbf{r}_2)\right]\mathrm{d}\mathbf{r}_3 = -\frac{2}{3}\Gamma_2(\mathbf{r}_1,\mathbf{r}_2). \tag{11}$$

By analogy with the classical Equation (1), we must change the variables of integration from $\mathbf{r}_3$ to $\mathbf{r}_3 - \mathbf{r}_1 = \mathbf{R}$, which corresponds to a shift of the origin of the reference frame, while the result depends only on the difference $\mathbf{r}_2 - \mathbf{r}_1 = \mathbf{r}$. Thus, by putting $g^{(3)} = \Gamma_3/n^3$ and $g = \Gamma_2/n^2$, we get, for the ferromagnetic HEF,

$$2g(r) + n\int\left[3g^{(3)}(\mathbf{r},\mathbf{R}) - g(r)\right]\mathrm{d}\mathbf{R} = 0. \tag{12}$$

This equation looks very similar to the classical Equation (1) for liquid argon. Evidently, the right-hand side of Equation (12) is 0 because $S(0)$ for the ground state of the HEF is 0 at both Hartree–Fock and correlated level. The other difference is the coefficent 3 of $g^{(3)}$, which is a consequence of indistinguishability of electrons.

4. Conclusions

Equation (12) generalises a known classical result to a quantum-mechanical Fermion system in its ground state. Although this result is established for a ferromagnetic HEF, the analogy with classical statistical mechanics suggests that, at least as a first approximation, Equation (12) could be used to relate $g^{(3)}$ to g also for an interacting Fermion system at $T = 0$ in which the two-body interaction is the same for any pair of particles.

A further interesting point is the relation of the pair function to the density. This appears in the right-hand side of the classical Equation (1) but not in (12) owing to the fact that in our HEF we have $S(0) = 0$. Numerous early workers considered a **k**-space treatment aimed at relating the structure factor $S(k)$ in the homogeneous electron liquid to the Fermi hole result $S_{FH}(k)$. Stoddart [5] has summarised such attempts by writing

$$\left[\frac{k^2}{2S(k)}\right]^2 = \left[\frac{k^2}{2S_{FH}(k)}\right]^2 + 4\pi n\left[1 + \frac{k^2}{2\pi}B(k)\right], \tag{13}$$

which can be viewed as a definition of the function $B(k)$. In an approximate **r**-space theory, Vashishta and Singwi [6] have related the Fourier transform $\mathcal{B}(r)$ of $B(k)$ to the total correlation function $h(r) = g(r) - 1$ plus its density derivative. In a recent paper, Amovilli and March [7] have shown that some progress in this direction can be achieved by considering the direct correlation function $c(r)$ related to $h(r)$ via the Ornstein–Zernike equation [8,9]. Amovilli and March worked again in **k**-space and their result suggests that there should exist a correlation between $\partial g(r)/\partial n$ for the homogeneous electron liquid and the direct correlation function $c(r, n)$.

Acknowledgements

N.H. March thanks Professors D. Van Dyck and D. Lamoen for making possible his continuing affiliation with the University of Antwerp, due to partial support by FWO-Vlaanderen under project G.0425.05. C. Amovilli and Á. Nagy acknowledge the Bilateral Scientific Cooperation between Italy and Hungary sponsored by Consiglio Nazionale delle Ricerche and Hungarian Academy of Sciences. Grant OTKA No. T029469 is gratefully acknowledged.

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