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Density-fluctuation approach to the classical plasma

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Abstract. In a classical fluid, whose potential energy may be expressed in terms of a pair potential possessing a Fourier transform, the potential of average force $U(r_{12})$ is closely related to an ensemble average of the reduced density fluctuation

$$\sum_{j=3}^{N} \exp(-i\mathbf{k}.\mathbf{r}_j).$$

A method is developed of evaluating this ensemble average, and the relationship of the latter to the three-particle distribution function is explained. The technique is applied to the electron plasma and $U(r_{12})$ is evaluated to second order in the standard plasma parameter $\epsilon = e^2k_D/k_BT$, a result, which, though not new, is comparatively easily derived, and the importance of the correct normalization of the radial distribution function

$$g(r_{12}) = \exp\left\{-\frac{U(r_{12})}{k_BT}\right\}$$

in this problem is stressed. Finally, the possibility of extending the results to values of ϵ where a series expansion is completely inappropriate is discussed.

1. Introduction

The density-fluctuation approach to a classical fluid is discussed in the first part of the paper, and attention is concentrated on the potential of average force $U(r_{12})$ defined through the radial distribution function $g(r_{12})$ by the equation

$$g(r_{12}) = \exp\left\{-\frac{U(r_{12})}{k_BT}\right\}.$$

It is shown how to write $U(r_{12})$ in terms of an ensemble average of the reduced density fluctuation

$$\sum_{j=3}^{N} \exp(-i\mathbf{k}.\mathbf{r}_j)$$

and a method of evaluating this ensemble average is developed. Since the latter is closely related to the three-particle distribution function, some insight is gained into this also. In the second part the technique is applied to the classical plasma.

The radial distribution function in an electron plasma has been discussed by a number of authors in recent years with a view to calculating the thermodynamic properties of the system beyond the Debye–Hückel limit. These investigations have used either diagrammatic techniques, starting from Mayer's cluster expansion (Abe 1959, Bowers and Salpeter 1960, De Witt 1965), or the Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy equation (Lamb and Burdick 1964, Gurnsey 1964, Fisher 1964, O'Neil and Rostocker 1965, Lie and Ichikawa 1966) and have resulted in a correlation energy which is correct to second order in the plasma parameter $\epsilon = e^2k_D/k_BT$, where k_D is the Debye wave number $(4\pi ne^2/k_BT)^{1/2}$, n being the number density of the electrons. To this order, the correlation energy is

$$\frac{E}{k_BT} = -\tfrac{1}{2}\epsilon - \tfrac{1}{4}\epsilon^2 \log \epsilon - \tfrac{1}{2}(\gamma - \tfrac{2}{3} + \tfrac{1}{2}\log 3)\epsilon^2 \tag{1}$$

where $\gamma = 0{\cdot}5772$ is the Euler constant and $-\frac{1}{2}\epsilon$ is the correlation energy within the Debye–Hückel approximation. An expression for the potential of average force to second order in ϵ is derived here, which, though not new, is comparatively easily obtained once the formalism is set up, and the importance of the correct normalization of the radial distribution function in this problem is stressed. Recently the radial distribution function and thermodynamic properties of a one-component plasma have been investigated, using a Monte Carlo method (Brush *et al.* 1966), over a very wide range of values of ϵ and the existence of a phase change predicted. The possibility of extending the present approach to large values of ϵ, where the type of expansion of equation (1) is completely inappropriate, is finally discussed.

2. Equation for the potential of average force

Let us consider a fluid of N particles in a box of volume V. The radial distribution function $g(r_{12})$ of a system of particles, whose potential energy can be expressed as a sum of pair potentials $\phi(r_{ij})$, is given by

$$g(r_{12}) = V^2 \int \exp\left\{-\frac{1}{2k_B T} \sum_{i,j(i\neq j)} \phi(r_{ij})\right\} d\mathbf{r}_3 \dots d\mathbf{r}_N$$
$$\times \left[\int \exp\left\{-\frac{1}{2k_B T} \sum_{i,j(i\neq j)} \phi(r_{ij})\right\} d\mathbf{r}_1 \dots d\mathbf{r}_N\right]^{-1}$$

in the limit N, $V \to \infty$, such that $N/V \to n$ and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. In this case it may be written

$$g(r_{12}) = V^2 \int \exp\Big(-\sum_{\mathbf{k}} v(k)[\exp(i\mathbf{k}.\mathbf{r}_{12}) + \{\exp(i\mathbf{k}.\mathbf{r}_1)+\exp(i\mathbf{k}.\mathbf{r}_2)\}\rho_{\mathbf{k}}'$$
$$+\tfrac{1}{2}\rho_{\mathbf{k}}'\rho_{\mathbf{k}}'^{*}]\Big)\, d\mathbf{r}_3 \dots d\mathbf{r}_N$$
$$\times \left[\int \exp\left\{-\frac{1}{2k_B T}\sum \phi(r_{ij})\right\} d\mathbf{r}_1 \dots d\mathbf{r}_N\right]^{-1} \tag{2}$$

where $v(k)$ is the Fourier transform of $\phi(r)/k_B T$ and

$$\rho_{\mathbf{k}}' = \sum_{j=3}^{N} \exp(-i\mathbf{k}.\mathbf{r}_j).$$

Hence

$$\nabla_1 g(r_{12}) = \left\{-i\sum_{\mathbf{k}} v(k)\exp(i\mathbf{k}.\mathbf{r}_{12})\mathbf{k} - i\sum_{\mathbf{k}} v(k)\exp(i\mathbf{k}.\mathbf{r}_1)\langle\rho_{\mathbf{k}}'\rangle\mathbf{k}\right\} g(r_{12}) \tag{3}$$

where

$$\langle\rho_{\mathbf{k}}'\rangle = \int \rho_{\mathbf{k}}' \exp\Big(-\sum_{\mathbf{k}} v(k)[\{\exp(i\mathbf{k}.\mathbf{r}_1)+\exp(i\mathbf{k}.\mathbf{r}_2)\}\rho_{\mathbf{k}}' + \tfrac{1}{2}\rho_{\mathbf{k}}'\rho_{\mathbf{k}}'^{*}]\Big)\, d\mathbf{r}_3 \dots d\mathbf{r}_N$$
$$\times \left[\int \exp\left\{-\frac{1}{2k_B T}\sum \phi(r_{ij})\right\} d\mathbf{r}_3 \dots d\mathbf{r}_N\right]^{-1}, \ \phi(r_{12}) \text{ now being omitted.} \tag{4}$$

Equation (3) is an equation for the potential average force since it may be written

$$\frac{\nabla_1 U(r_{12})}{k_B T} = \sum_{\mathbf{k}} iv(k)\exp(i\mathbf{k}.\mathbf{r}_{12})\mathbf{k} + \sum_{\mathbf{k}} iv(k)\exp(i\mathbf{k}.\mathbf{r}_1)\langle\rho_{\mathbf{k}}'\rangle\mathbf{k}. \tag{5}$$

The evaluation of $U(r_{12})$ therefore requires a calculation of the quantity $\langle\rho_{\mathbf{k}}'\rangle$, and this problem will now be discussed. If we define

$$\alpha(n) = \exp(i\mathbf{n}.\mathbf{r}_1) + \exp(i\mathbf{n}.\mathbf{r}_2)$$

then we have

$$\int \sum_{j=3}^{N} i\exp(-i\mathbf{k}.\mathbf{r}_j)\mathbf{k}.\nabla_j \exp\Big[-\sum_{\mathbf{n}} v(n)\{\alpha(n)\rho_{\mathbf{n}}{}'+\tfrac{1}{2}\rho_{\mathbf{n}}{}'\rho_{\mathbf{n}}{}'^*\}\Big]\,d\mathbf{r}_3\ldots d\mathbf{r}_N$$

$$\times\Big[\int \exp\Big\{-\frac{1}{2k_{\mathrm{B}}T}\sum \phi(r_{ij})\Big\}\,d\mathbf{r}_3\ldots d\mathbf{r}_N\Big]^{-1}$$

$$= -\sum_{\mathbf{n}} v(n)\alpha(n)\langle\rho'_{\mathbf{k}+\mathbf{n}}\rangle\mathbf{k}.\mathbf{n}-\sum_{\mathbf{n}} v(n)\langle\rho'_{\mathbf{k}+\mathbf{n}}\rho_{\mathbf{n}}{}'^*\rangle\mathbf{k}.\mathbf{n}.$$

The numerator on the left-hand side may be written

$$\int \sum_{j=3}^{N} \nabla_j.\Big\{i\mathbf{k}\exp(-i\mathbf{k}.\mathbf{r}_j)\exp\Big[-\sum_{\mathbf{n}} v(n)\{\alpha(n)\rho_{\mathbf{n}}{}'+\tfrac{1}{2}\rho_{\mathbf{n}}{}'\rho_{\mathbf{n}}{}'^*\}\Big]\Big\}\,d\mathbf{r}_3\ldots d\mathbf{r}_N-k^2\langle\rho_{\mathbf{k}}{}'\rangle$$

and, since the first term may be converted to a surface integral and hence shown to be zero, we have the equation

$$\langle\rho_{\mathbf{k}}{}'\rangle = \frac{1}{k^2}\sum_{\mathbf{n}} v(n)\alpha(n)\langle\rho'_{\mathbf{k}+\mathbf{n}}\rangle\mathbf{k}.\mathbf{n}+\frac{1}{k^2}\sum_{\mathbf{n}} v(n)\langle\rho'_{\mathbf{k}+\mathbf{n}}\rho_{\mathbf{n}}{}'^*\rangle\mathbf{k}.\mathbf{n}. \tag{6}$$

It is more convenient at this stage to define the quantity

$$\langle\tilde{\rho}_{\mathbf{k}}\rangle = \exp(i\mathbf{k}.\mathbf{r}_1)\langle\rho_{\mathbf{k}}{}'\rangle$$

and then equation (5) becomes

$$\frac{\nabla_1 U(r_{12})}{k_{\mathrm{B}}T} = \sum_{\mathbf{k}} iv(k)\exp(i\mathbf{k}.\mathbf{r}_{12})\mathbf{k}+\sum_{\mathbf{k}} iv(k)\langle\tilde{\rho}_{\mathbf{k}}\rangle\mathbf{k} \tag{7}$$

and instead of (6) we have

$$\langle\tilde{\rho}_{\mathbf{k}}\rangle = \frac{1}{k^2}\sum_{\mathbf{n}} v(n)\{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\}\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\rangle\mathbf{k}.\mathbf{n}+\frac{1}{k^2}\sum_{\mathbf{n}} v(n)\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}_{\mathbf{n}}{}^*\rangle\mathbf{k}.\mathbf{n}. \tag{8}$$

The quantity $\langle\tilde{\rho}_{\mathbf{k}}\rangle$ is a function of $\mathbf{k}$, r_{12} and the angle between them, and its connection with the three-particle distribution function will now be clarified.

The three-particle distribution function of the system, $g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, is given by

$$g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = V\int \exp\Big\{-\frac{1}{2k_{\mathrm{B}}T}\sum_{i,j(i\neq j)}\phi(r_{ij})\Big\}\,d\mathbf{r}_4\ldots d\mathbf{r}_N$$

$$\times\Big[\int \exp\Big\{-\frac{1}{2k_{\mathrm{B}}T}\sum_{i,j(i\neq j)}\phi(r_{ij})\Big\}\,d\mathbf{r}_1\ldots d\mathbf{r}_N\Big]^{-1} \tag{9}$$

and hence, using the definition of the radial distribution function given earlier, we have

$$\frac{g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{g(r_{12})} = V\int \exp\Big\{-\frac{1}{2k_{\mathrm{B}}T}\sum_{i,j(i\neq j)}\phi(r_{ij})\Big\}\,d\mathbf{r}_4\ldots d\mathbf{r}_N$$

$$\times\Big[\int \exp\Big\{-\frac{1}{2k_{\mathrm{B}}T}\sum_{i,j(i\neq j)}\phi(r_{ij})\Big\}\,d\mathbf{r}_3\ldots d\mathbf{r}_N\Big]^{-1}. \tag{10}$$

For a fluid the three-particle distribution function may be written as $g(\mathbf{r}, \mathbf{s})$, where $\mathbf{r} = \mathbf{r}_{12}$

and $\mathbf{s} = \mathbf{r}_{13}$, and we may therefore write

$$\begin{aligned}\frac{g(\mathbf{r},\mathbf{s})}{g(r)} &= V\int \delta(\mathbf{r}_1-\mathbf{r}_3-\mathbf{s})\exp\left\{-\frac{1}{2k_{\mathrm{B}}T}\sum_{i,j(i\neq j)}\phi(r_{ij})\right\}d\mathbf{r}_3\ldots d\mathbf{r}_N \\ &\quad\times\left[\int\exp\left\{-\frac{1}{2k_{\mathrm{B}}T}\sum_{i,j(i\neq j)}\phi(r_{ij})\right\}d\mathbf{r}_3\ldots d\mathbf{r}_N\right]^{-1} \\ &= \frac{V}{N-2}\sum_{j=3}^{N}\int\delta(\mathbf{r}_1-\mathbf{r}_j-\mathbf{s})\exp\left\{-\frac{1}{2k_{\mathrm{B}}T}\sum_{i,j(i\neq j)}\phi(r_{ij})\right\}d\mathbf{r}_3\ldots d\mathbf{r}_N \\ &\quad\times\left[\int\exp\left\{-\frac{1}{2k_{\mathrm{B}}T}\sum_{i,j(i\neq j)}\phi(r_{ij})\right\}d\mathbf{r}_3\ldots d\mathbf{r}_N\right]^{-1} \qquad (11)\end{aligned}$$

the last step following because we may choose the third particle from any in the system apart from 1 and 2. If we express the delta function as the Fourier series

$$\frac{1}{V}\sum_{\mathbf{k}}\exp\{i\mathbf{k}.(\mathbf{r}_1-\mathbf{r}_j-\mathbf{s})\}$$

it follows immediately from (4) that

$$\frac{g(\mathbf{r},\mathbf{s})}{g(r)} = \frac{1}{N-2}\sum_{\mathbf{k}}\langle\tilde{\rho}_{\mathbf{k}}\rangle\exp(-i\mathbf{k}.\mathbf{s})$$

and since $\langle\tilde{\rho}_0\rangle = N-2$ we have

$$\frac{g(\mathbf{r}_{12},\mathbf{r}_{13})}{g(r_{12})} = 1+\frac{1}{N-2}\sum_{\mathbf{k}\neq 0}\langle\tilde{\rho}_{\mathbf{k}}\rangle\exp(-i\mathbf{k}.\mathbf{r}_{13}). \qquad (12)$$

$ng(\mathbf{r}_{12},\mathbf{r}_{13})\,d\mathbf{r}_3/g(r_{12})$ may be interpreted as the number of particles in volume element $d\mathbf{r}_3$ when particle 1 is at $\mathbf{r}_1$ and particle 2 at $\mathbf{r}_2$.

3. Application to the electron plasma

We consider a system of N electrons in the presence of a neutralizing background of positive charge in a box of volume V, and for this problem

$$v(k) = \frac{4\pi e^2}{k_{\mathrm{B}}TVk^2}$$

the $k = 0$ component cancelling with the background of positive charge.

3.1. *Random-phase approximation*

It should be noted that $\langle\tilde{\rho}_0\rangle = N-2$, though we shall in future ignore the 2, and that the random-phase approximation consists in extracting the terms on the right-hand side of equation (8) with $\mathbf{n} = -\mathbf{k}$. Hence, within this approximation,

$$\langle\tilde{\rho}_{\mathbf{k}}\rangle = -Nv(k)\{1+\exp(i\mathbf{k}.\mathbf{r}_{12})\}-Nv(k)\langle\tilde{\rho}_{\mathbf{k}}\rangle$$

so that

$$\langle\tilde{\rho}_{\mathbf{k}}\rangle_{\mathrm{RPA}} = -\frac{Nv(k)\{1+\exp(i\mathbf{k}.\mathbf{r}_{12})\}}{1+Nv(k)}. \qquad (13)$$

Using equation (7), it follows immediately that

$$\frac{U(r_{12})}{k_{\mathrm{B}}T} = \sum_{\mathbf{k}} v(k)\exp(i\mathbf{k}.\mathbf{r}_{12})\left\{1-\frac{Nv(k)}{1+Nv(k)}\right\}$$

and with the usual substitution

$$\sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3}\int d\mathbf{k}$$

we have

$$\frac{U(r_{12})}{k_B T} = \frac{e^2}{k_B T}\frac{1}{(2\pi)^3}\int d\mathbf{k}\exp(i\mathbf{k}.\mathbf{r}_{12})\frac{4\pi}{k^2+k_D{}^2} = \frac{e^2}{k_B T}\frac{\exp(-k_D r_{12})}{r_{12}}.$$

The three-particle distribution function may also be immediately evaluated and, in fact,

$$\frac{g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{g(r_{12})} = 1-\frac{e^2}{k_B T}\frac{\exp(-k_D|\mathbf{r}_1-\mathbf{r}_3|)}{|\mathbf{r}_1-\mathbf{r}_3|}-\frac{e^2}{k_B T}\frac{\exp(-k_D|\mathbf{r}_2-\mathbf{r}_3|)}{|\mathbf{r}_2-\mathbf{r}_3|} \tag{14}$$

a result which clearly becomes invalid if the third particle closely approaches either particle 1 or 2, but which will have some significance asymptotically. It is the Debye–Hückel approximation to this three-particle distribution function. However, the corresponding radial distribution function

$$g(r_{12}) = \exp\left\{-\frac{e^2}{k_B T}\frac{\exp(-k_D r_{12})}{r_{12}}\right\}$$

sometimes referred to as the non-linear Debye–Hückel result, does not suffer from this defect as r_{12} becomes small. In terms of the dimensionless quantity $x = k_D r$ it becomes

$$g(x) = \exp\left(-\epsilon\frac{e^{-x}}{x}\right).$$

The correlation energy is given by

$$\frac{E}{k_B T} = \frac{n}{2k_B T}\int d\mathbf{r}\frac{e^2}{r}\{g(r)-1\}$$

and with the above approximation for $g(r)$ we have, to order ϵ^2,

$$\frac{E}{k_B T} = -\tfrac{1}{2}\epsilon-\tfrac{1}{4}\epsilon^2\log\epsilon-\tfrac{1}{2}(\gamma+\tfrac{1}{2}\log 2-\tfrac{3}{4})\epsilon^2. \tag{15}$$

A property of the radial distribution function, which appears to receive little attention is the normalization condition, namely

$$n\int d\mathbf{r}\{g(r)-1\} = -1.$$

This result is a consequence of the model of a plasma we are considering, and guarantees the physical requirement that there must be just sufficient positive charge around any one electron for the screening to be complete. A more extensive discussion of this point will be given in appendix 1. For the present radial distribution function this condition is not satisfied, and the normalization integral is always greater than -1. To order ϵ^2,

$$n\int d\mathbf{r}\{g(r)-1\} = -1+\tfrac{1}{4}\epsilon+\tfrac{1}{6}(\log\epsilon+\log 3+2\gamma-\tfrac{11}{6})\epsilon^2.$$

If we insist on the correct normalization of $g(r)-1$ before using it to estimate the energy, then, to order ϵ^2, the result is

$$\frac{E}{k_B T} = -\tfrac{1}{2}\epsilon-\tfrac{1}{4}\epsilon^2\log\epsilon-\tfrac{1}{2}(\gamma+\tfrac{1}{2}\log 2-\tfrac{1}{2})\epsilon^2. \tag{16}$$

The exact coefficient of ϵ^2 from (1) is $-0{\cdot}23$, that given by (15) is $-0{\cdot}087$ and after normalization it becomes $-0{\cdot}21$. In fact, this simple expression for $g(r)$ when normalized gives surprisingly good results for the energy over a wide range of ϵ, as the following table shows, where a comparison is made with the recent Monte Carlo calculations of Brush *et al.*

Table 1. Correlation energy in units of $k_B T$

ϵ	Debye–Hückel	Normalization	Normalized Debye–Hückel	Monte Carlo	Percus–Yevick
0·01936	−0·00934	0·995	−0·00939	−0·0128	−0·008
0·05477	−0·0255	0·988	−0·0258	−0·0270	−0·020
1·7321	−0·468	0·871	−0·577	−0·579	−0·539
4·899	−0·925	0·673	−1·37	−1·338	−1·448
6·844	−1·128	0·454	−1·81	−1·729	−1·903

The results from the Percus–Yevick equation have also been taken from the same reference. Of course, if we regard the radial distribution function after normalization as $1+\{g(r)-1\}_{\text{normalized}}$, then it will have the defect of becoming negative at the origin, increasingly so as ϵ increases; but as far as the energy is concerned this seems to be relatively unimportant.

The non-linear Debye–Hückel result derives from a calculation of $U(r_{12})$ to first order in ϵ; to obtain results to second order, and hence the exact second-order calculation of the energy, that is equation (1), a more careful analysis of equation (8) is required and this will now be discussed.

3.2. *Second-order approximation to $U(r_{12})$*

Equation (8) may be written

$$\langle\tilde{\rho}_{\mathbf{k}}\rangle = -\frac{Nv(k)\{1+\exp(i\mathbf{k}.\mathbf{r}_{12})\}}{1+Nv(k)} + \frac{1}{1+Nv(k)}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}} v(n)\{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\}\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\rangle\mathbf{k}.\mathbf{n} + \frac{1}{1+Nv(k)}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}} v(n)\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}_{\mathbf{n}}^*\rangle\mathbf{k}.\mathbf{n}. \tag{17}$$

It is tempting to decouple the last term and write it as $\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\rangle\langle\tilde{\rho}_{\mathbf{n}}^*\rangle$, and to attempt to solve the resulting integral equation by iteration. This leads to an expansion of $U(r_{12})$ in terms of ϵ, but does not yield all of the terms up to second order in ϵ. In fact, we obtain as the first term beyond the random-phase approximation

$$-\frac{1}{1+Nv(k)}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}}\frac{v(n)\{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\}}{1+Nv(n)}\frac{Nv(|\mathbf{k}+\mathbf{n}|)[1+\exp\{i(\mathbf{k}+\mathbf{n}).\mathbf{r}_{12}\}]}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\mathbf{k}.\mathbf{n}. \tag{18}$$

This consists of a term independent of r_{12} (which integrates to zero when substituted in (7)) and the following expression:

$$-\frac{1}{1+Nv(k)}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}}\mathbf{k}.\mathbf{n}\left[\frac{Nv(|\mathbf{k}+\mathbf{n}|)}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\frac{v(n)}{1+Nv(n)}\{\exp(i\mathbf{k}.\mathbf{r}_{12})+\exp(-i\mathbf{n}.\mathbf{r}_{12})\} + \frac{Nv(|\mathbf{k}+\mathbf{n}|)}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\frac{v(n)}{1+Nv(n)}\exp\{i(\mathbf{k}+\mathbf{n}).\mathbf{r}_{12}\}\right]. \tag{19}$$

If in the last term we make the substitution $\mathbf{k}+\mathbf{n} = -\mathbf{s}$, it becomes

$$-\sum_{\mathbf{s}}\mathbf{k}.(\mathbf{s}+\mathbf{k})\frac{Nv(s)}{1+Nv(s)}\frac{v(|\mathbf{k}+\mathbf{s}|)}{1+Nv(|\mathbf{k}+\mathbf{s}|)}\exp(-i\mathbf{s}.\mathbf{r}_{12})$$

and the first term cancels with the second term in (19), which then becomes

$$-\frac{1}{1+Nv(k)}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}}\left\{\mathbf{k}.\mathbf{n}\frac{Nv(|\mathbf{k}+\mathbf{n}|)}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\frac{v(n)}{1+Nv(n)}\exp(i\mathbf{k}.\mathbf{r}_{12})\right.$$
$$\left.-k^2\frac{Nv(|\mathbf{k}+\mathbf{n}|)}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\frac{v(n)}{1+Nv(n)}\exp(-i\mathbf{n}.\mathbf{r}_{12})\right\}. \tag{20}$$

It is not difficult to show that the contribution this term makes to $U(r_{12})/k_BT$ is given by

$$-2\sum_{\mathbf{k}}\frac{v(k)}{1+Nv(k)}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}}\mathbf{k}.\mathbf{n}\frac{Nv(|\mathbf{k}+\mathbf{n}|)}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\frac{v(n)}{1+Nv(n)}\exp(i\mathbf{k}.\mathbf{r}_{12}). \tag{21}$$

Replacing the summations by integrals, we obtain

$$\epsilon^2\frac{1}{4\pi}\int d\mathbf{y}\frac{e^{-y}}{y}\frac{\exp(-2|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|^2} \tag{22}$$

where, as before, $x = k_D r_{12}$. This last step follows immediately when we realize that

$$\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}}\mathbf{k}.\mathbf{n}\frac{Nv(|\mathbf{k}+\mathbf{n}|)}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\frac{v(n)}{1+Nv(n)}\rightarrow\frac{k_D^4}{n(4\pi)^2}\left\{\frac{1}{(2\pi)^3k^2}\int d\mathbf{n}\,\mathbf{k}.\mathbf{n}\frac{4\pi}{|\mathbf{k}+\mathbf{n}|^2+k_D^2}\frac{4\pi}{n^2+k_D^2}\right\}$$

and that

$$\frac{1}{(2\pi)^3k^2}\int d\mathbf{n}\,\mathbf{k}.\mathbf{n}\frac{4\pi}{|\mathbf{k}+\mathbf{n}|^2+k_D^2}\frac{4\pi}{n^2+k_D^2} = -\frac{2\pi}{k}\tan^{-1}\left(\frac{k}{2k_D}\right)$$

the Fourier transform of $\exp(-2k_D r)/r^2$.

To include all of the second-order terms, however, we must evaluate the last term in equation (17) more accurately. The details are given in appendix 2, where it is shown by decoupling at a later stage that

$$\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}_{\mathbf{n}}^*\rangle \simeq -\frac{Nv(n)\{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\}}{1+Nv(n)}\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\rangle-\frac{\langle\tilde{\rho}_{\mathbf{k}}\rangle}{1+Nv(n)}\frac{1}{1+Nv(|\mathbf{k}+\mathbf{n}|)}. \tag{23}$$

Replacing this expression in (17) and again solving by iteration starting with the random-phase value of $\langle\tilde{\rho}_{\mathbf{k}}\rangle$, we obtain, instead of (18),

$$-\frac{1}{1+Nv(k)}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}}\frac{v(n)\{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\}}{1+Nv(n)}\frac{Nv(|\mathbf{k}+\mathbf{n}|)[1+\exp\{i(\mathbf{k}+\mathbf{n}).\mathbf{r}_{12}\}}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\mathbf{k}.\mathbf{n}$$
$$+\frac{Nv(k)\{1+\exp(i\mathbf{k}.\mathbf{r}_{12})\}}{\{1+Nv(k)\}^2}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}}\frac{v(n)}{1+Nv(n)}\frac{1}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\mathbf{k}.\mathbf{n}. \tag{24}$$

The first term, of course, is that given in (18), but the second one is new and the contribution it makes to $U(r_{12})/k_BT$ through equation (7) is

$$\sum_{\mathbf{k}}\frac{Nv^2(k)}{\{1+Nv(k)\}^2}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}}\mathbf{k}.\mathbf{n}\frac{v(n)}{1+Nv(n)}\frac{1}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\exp(i\mathbf{k}.\mathbf{r}_{12})$$
$$= -\frac{\epsilon^2}{32\pi^2}\int\int d\mathbf{y}\,d\mathbf{z}\frac{e^{-y}}{y}\frac{\exp(-2|\mathbf{y}-\mathbf{z}|)}{|\mathbf{y}-\mathbf{z}|^2}\frac{\exp(-|\mathbf{z}-\mathbf{x}|)}{|\mathbf{z}-\mathbf{x}|}. \tag{25}$$

Therefore, to second order in ϵ, we have

$$\frac{U(x)}{k_B T} = \epsilon \frac{e^{-x}}{x} + \frac{\epsilon^2}{4\pi} \int d\mathbf{y} \frac{e^{-y}}{y} \frac{\exp(-2|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|^2}$$
$$- \frac{\epsilon^2}{32\pi^2} \int \int d\mathbf{y}\, d\mathbf{z} \frac{e^{-y}}{y} \frac{\exp(-2|\mathbf{y}-\mathbf{z}|)}{|\mathbf{y}-\mathbf{z}|^2} \frac{\exp(-|\mathbf{z}-\mathbf{x}|)}{|\mathbf{z}-\mathbf{x}|}$$
$$= \epsilon \frac{e^{-x}}{x} + \lambda_1(x) + \lambda_2(x). \tag{26}$$

This is the expression obtained by Bowers and Salpeter, and the correlation energy to order ϵ^2 is given by

$$\tfrac{1}{2} \int_0^\infty dx\, x \left\{ \exp\left(-\epsilon \frac{e^{-x}}{x} \right) - 1 \right\} - \tfrac{1}{2} \int_0^\infty dx\, x \{ \lambda_1(x) + \lambda_2(x) \}.$$

The contribution from the first term has been given in equation (15) and the remaining contributions are

$$\tfrac{1}{2} \int_0^\infty dx\, x\lambda_1(x) = -\tfrac{1}{2}\epsilon^2(\log 3 - \log 2)$$

and

$$\tfrac{1}{2} \int_0^\infty dx\, x\lambda_2(x) = \tfrac{1}{4}\epsilon^2(\log 3 - \log 2 - \tfrac{1}{6}).$$

Together they give the exact result quoted in equation (1).

It is quickly shown that with the result (26) the normalization integral is correct to order ϵ^2, that is

$$n \int d\mathbf{r} \{ g(r) - 1 \} = -1 + O(\epsilon^2).$$

3.3. *Extension to large values of* ϵ

Recently Brush *et al.*, using a Monte Carlo method, have investigated the radial distribution function and thermodynamic properties of a one-component plasma over a wide range of values of ϵ. For the range of values they consider it is more appropriate to introduce the dimensionless parameter $\Gamma = e^2/r_s k_B T$, where r_s, the radius of a sphere containing one electron, is given by

$$\frac{1}{n} = \tfrac{4}{3}\pi r_s^3$$

and to express distances in terms of r_s rather than k_D^{-1} ($\epsilon = \sqrt{3}\Gamma^{3/2}$). For $\Gamma \sim 2$ the radial distribution function ceases to be monotonic, which is characteristic of the Debye–Hückel approximation, and begins to show oscillations due to the onset of short-range order.

If we start from the exact result (17), the simplest approximation in an attempt to extend the present approach to high values of Γ is to decouple the last term, that is to write $\langle \tilde{\rho}_{\mathbf{k}+\mathbf{n}} \tilde{\rho}_{\mathbf{n}}^* \rangle$ as $\langle \tilde{\rho}_{\mathbf{k}+\mathbf{n}} \rangle \langle \tilde{\rho}_{\mathbf{n}}^* \rangle$, so that the equation becomes

$$\langle \tilde{\rho}_{\mathbf{k}} \rangle = \frac{-Nv(k)\{1+\exp(i\mathbf{k}.\mathbf{r}_{12})\}}{1+Nv(k)} + \frac{1}{1+Nv(k)} \frac{1}{k^2} \sum_{\mathbf{n} \neq -\mathbf{k}} v(n) \{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\} \langle \tilde{\rho}_{\mathbf{k}+\mathbf{n}} \rangle \mathbf{k}.\mathbf{n}$$
$$+ \frac{1}{1+Nv(k)} \frac{1}{k^2} \sum_{\mathbf{n} \neq -\mathbf{k}} v(n) \langle \tilde{\rho}_{\mathbf{k}+\mathbf{n}} \rangle \langle \tilde{\rho}_{\mathbf{n}}^* \rangle \mathbf{k}.\mathbf{n}. \tag{27}$$

The second term on the right-hand side of (17) arises from the interaction of particles 1 and 2 with the other particles in the system, whilst the last term arises from the mutual interaction of these particles. If, after decoupling, we replace $\langle\tilde{\rho}_{\mathbf{n}}{}^*\rangle$ by its random-phase value, then (27) becomes

$$\langle\tilde{\rho}_{\mathbf{k}}\rangle = \frac{-Nv(k)\{1+\exp(i\mathbf{k}.\mathbf{r}_{12})\}}{1+Nv(k)} + \frac{1}{1+Nv(k)}\frac{1}{k^2}\sum_{\mathbf{n}\neq-\mathbf{k}}\frac{v(n)}{1+Nv(n)}\{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\}\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\rangle\mathbf{k}.\mathbf{n}.$$

Thus we see that the decoupling process approximately takes into account the mutual interaction by assuming that its effect is to screen the interaction between particles 1 and 2 and the rest of the system, since

$$\frac{Nv(n)}{1+Nv(n)} = \frac{k_{\mathrm{D}}{}^2}{n^2+k_{\mathrm{D}}{}^2}.$$

It is hoped to discuss in a subsequent paper the consequences of this approximation by attempting a numerical solution of equation (27).

4. Conclusions

The density-fluctuation approach appears to be an extremely useful way of discussing the equilibrium properties of a fluid with long-range interactions. The method involves the calculation of an ensemble average of the reduced density fluctuation

$$\sum_{j=3}^{N}\exp(-i\mathbf{k}.\mathbf{r}_j)$$

and, since this is related to the two-particle and three-particle distribution functions, information is obtained about both.

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Appendix 1

The result

$$n\int d\mathbf{r}\{g(r)-1\} = -1$$

is a consequence of the model of a plasma we have chosen, namely electrons plus neutralizing background of positive charge, and can be seen from the following argument. The radial distribution function for a one-component system, whose potential energy may be expressed as a sum of pair potentials $\phi(r)$, has the well-known property that

$$n\int d\mathbf{r}\{g(r)-1\} = -1+k_{\mathrm{B}}T\left(\frac{\partial n}{\partial p'}\right)_T$$

where the pressure p' is that given by the virial theorem,

$$p' = nk_{\mathrm{B}}T-\tfrac{1}{6}n^2\int d\mathbf{r}\, rg(r)\frac{d\phi}{dr}.$$

In this problem when we make the substitution

$$\sum_{\mathbf{k}\neq0}\to\frac{V}{(2\pi)^3}\int d\mathbf{k}$$

in the evaluation of $g(r)$ we are calculating the latter for a Coulomb potential $\phi(r) = e^2/r$, and the isothermal compressibility $(1/n)(\partial n/\partial p')_T$ in the above equation is that for a system of electrons without the background of positive charge. From the virial result, if we take the asymptotic limit 1 from $g(r)$, the pressure p' contains the term

$$-\tfrac{1}{6}n^2 \int d\mathbf{r}\, r \frac{d\phi}{dr}$$

and $(\partial p'/\partial n)_T$ the term

$$-\tfrac{1}{3}n \int d\mathbf{r}\, r \frac{d\phi}{dr}$$

both of which are infinite as $V \to \infty$. Hence

$$\left(\frac{\partial n}{\partial p'}\right)_T \to 0$$

in this limit. However, in evaluating the usual expressions for the pressure p or energy E of the system of electrons and background charge we must carefully remove the $k = 0$ component in the Fourier transform of the potential $\phi(r)$, and this leads to the well-known results for this model, namely

$$p = nk_B T - \tfrac{1}{6}n^2 \int d\mathbf{r}\, r\{g(r)-1\}\frac{d\phi}{dr}$$

$$\frac{E}{N} = \tfrac{3}{2}k_B T + \tfrac{1}{2}n \int d\mathbf{r}\{g(r)-1\}\,\phi(r).$$

Appendix 2

To obtain the potential of average force to second order in ϵ, the evaluation of the expression $\langle \tilde{\rho}_{\mathbf{k}+\mathbf{n}}\, \tilde{\rho}_{\mathbf{n}}^* \rangle$ is required. By repeating the process used to obtain equation (6), it may quickly be shown that

$$\langle \rho_{\mathbf{p}}'\rho_{\mathbf{n}}'^* \rangle = \frac{1}{n^2}\mathbf{p}.\mathbf{n}\langle \rho_{\mathbf{p}-\mathbf{n}}' \rangle - \frac{1}{n^2}\sum_{\mathbf{l}} v(l)\alpha(l)\langle \rho_{\mathbf{l}-\mathbf{n}}'\rho_{\mathbf{p}}' \rangle \mathbf{n}.\mathbf{l}$$
$$-\frac{1}{n^2}\sum_{\mathbf{l}} v(l)\langle \rho_{\mathbf{l}-\mathbf{n}}'\rho_{\mathbf{l}}'^*\rho_{\mathbf{p}} \rangle \mathbf{n}.\mathbf{l}. \tag{A1}$$

Some of the individual terms under the summation signs are of order N and must be treated separately. Hence, with $\mathbf{p} = \mathbf{k}+\mathbf{n}$, we have

$$\langle \rho_{\mathbf{k}+\mathbf{n}}'\rho_{\mathbf{n}}'^* \rangle = \frac{1}{n^2}\mathbf{n}.(\mathbf{k}+\mathbf{n})\langle \rho_{\mathbf{k}}' \rangle - Nv(n)\alpha(n)\langle \rho_{\mathbf{k}+\mathbf{n}}' \rangle$$
$$+\frac{1}{n^2}\mathbf{n}.\mathbf{k}v(k)\alpha(-k)\langle \rho_{\mathbf{k}+\mathbf{n}}'\rho_{\mathbf{k}+\mathbf{n}}'^* \rangle - Nv(n)\langle \rho_{\mathbf{k}+\mathbf{n}}'\rho_{\mathbf{n}}'^* \rangle$$
$$-\frac{1}{n^2}\mathbf{n}.(\mathbf{k}+\mathbf{n})v(|\mathbf{k}+\mathbf{n}|)\langle \rho_{\mathbf{k}}'\rho_{\mathbf{k}+\mathbf{n}}'\rho_{\mathbf{k}+\mathbf{n}}'^* \rangle + \frac{1}{n^2}\mathbf{n}.\mathbf{k}v(k)\langle \rho_{\mathbf{k}}'\rho_{\mathbf{k}+\mathbf{n}}'\rho_{\mathbf{k}+\mathbf{n}}'^* \rangle$$
$$-\frac{1}{n^2}\sum_{\mathbf{l}\neq\mathbf{n},-\mathbf{k}} v(l)\alpha(l)\langle \rho_{\mathbf{l}-\mathbf{n}}'\rho_{\mathbf{p}}' \rangle \mathbf{n}.\mathbf{l} - \frac{1}{n^2}\sum_{\mathbf{l}\neq\mathbf{n},-\mathbf{k},\mathbf{k}+\mathbf{n}} v(l)\langle \rho_{\mathbf{l}-\mathbf{n}}'\rho_{\mathbf{l}}'^*\rho_{\mathbf{p}}' \rangle. \tag{A2}$$

It should be noted that

$$\langle \rho_{\mathbf{p}}'\rho_{\mathbf{q}}'^* \rangle \sim \mathrm{O}(N) \quad \text{if} \quad \mathbf{p} = \mathbf{q}$$

and O(1) otherwise. Since we are interested only in terms up to second order in ϵ, we may drop the expressions involving a summation over a third wave number $\mathbf{l}$ since these give a higher-order contribution. We shall also decouple the last two remaining terms in (A2), and therefore

$$\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}_{\mathbf{n}}{}^*\rangle = -\frac{Nv(n)}{1+Nv(n)}\{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\}\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\rangle+\frac{1}{1+Nv(n)}\frac{1}{n^2}\{\mathbf{n}.(\mathbf{k}+\mathbf{n})\langle\tilde{\rho}_{\mathbf{k}}\rangle$$
$$-\mathbf{n}.(\mathbf{k}+\mathbf{n})v(|\mathbf{k}+\mathbf{n}|)\langle\tilde{\rho}_{\mathbf{k}}\rangle\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}^*_{\mathbf{k}+\mathbf{n}}\rangle+\mathbf{n}.\mathbf{k}v(k)\langle\tilde{\rho}_{\mathbf{k}}\rangle\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}^*_{\mathbf{k}+\mathbf{n}}\rangle\}$$
$$+\frac{1}{1+Nv(n)}\frac{1}{n^2}\mathbf{n}.\mathbf{k}v(k)\{1+\exp(i\mathbf{k}.\mathbf{r}_{12})\}\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}^*_{\mathbf{k}+\mathbf{n}}\rangle. \tag{A3}$$

If we refer back to equation (A1) with $\mathbf{n} = \mathbf{p}$, it follows immediately that within the random-phase approximation

$$\langle\rho_{\mathbf{p}}{}'\rho_{\mathbf{p}}{}'^*\rangle = \frac{N}{1+Nv(p)}$$

or, with $\mathbf{p} = \mathbf{k}+\mathbf{n}$, the expression relevant to (A3) becomes

$$\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}^*_{\mathbf{k}+\mathbf{n}}\rangle = \frac{N}{1+Nv(|\mathbf{k}+\mathbf{n}|)}$$

which is sufficiently accurate to obtain results correct to order ϵ^2. With this further approximation, (A3) becomes

$$\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}_{\mathbf{n}}{}^*\rangle \simeq -\frac{Nv(n)\{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\}}{1+Nv(n)}\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\rangle-\frac{\langle\tilde{\rho}_{\mathbf{k}}\rangle}{1+Nv(n)}\frac{1}{1+Nv(|\mathbf{k}+\mathbf{n}|)}$$
$$+\frac{1+Nv(k)}{1+Nv(n)}\frac{1}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\frac{1}{n^2}(\langle\tilde{\rho}_{\mathbf{k}}\rangle-\langle\tilde{\rho}_{\mathbf{k}}\rangle_{\mathrm{RPA}})\mathbf{k}.\mathbf{n}.$$

The last term is clearly of the same order as the terms which have been neglected, since to first order $\langle\tilde{\rho}_{\mathbf{k}}\rangle = \langle\tilde{\rho}_{\mathbf{k}}\rangle_{\mathrm{RPA}}$, so that we may drop it at this stage and

$$\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\tilde{\rho}_{\mathbf{n}}{}^*\rangle \simeq -\frac{Nv(n)\{1+\exp(-i\mathbf{n}.\mathbf{r}_{12})\}}{1+Nv(n)}\langle\tilde{\rho}_{\mathbf{k}+\mathbf{n}}\rangle-\frac{1}{1+Nv(|\mathbf{k}+\mathbf{n}|)}\frac{\langle\tilde{\rho}_{\mathbf{k}}\rangle}{1+Nv(n)} \tag{A4}$$

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