CORRELATION OF POSITION FOR THE IDEAL QUANTUM GAS

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1. Introduction*

It is well known that in quantum theory the particles of a gas cannot be considered as independent even in the limiting case of zero interaction (ideal gas). As a consequence of the symmetry properties of the wave function, the space coordinates of the particles are correlated in the sense of an apparent repulsion in the case of Fermi-Dirac statistics and of an apparent attraction in the case of Bose-Einstein statistics. The explicit quantitative form of the correlation has been given for temperatures high compared to the degeneracy temperature [1] and for the fully degenerate Fermi gas [2]. In the following we shall discuss the general case of the ideal gas without interaction and the connection between correlation of position, density fluctuation and scattering properties of the gas.

The procedure followed is a slight generalization of a method used by Heisenberg [3].

2. General relations

We consider the density in six dimensional coordinate space (pair density) which we denote by $\rho_2(\bar{r}, \bar{r}')$. For a gas, this quantity can only be a function of the absolute value of the distance between the particles and may hence be written

$$\rho_2(\bar{r}, \bar{r}') = \rho^2 W(|\bar{r} - \bar{r}'|) . \tag{1}$$

Here ρ is the ordinary density (number of particles per unit volume) and $\rho W(R)$ the density at distance R from a given particle. If the particles are independent, $W(R) = 1$; in the general case, $W(R)$ tends to 1 for large R. The function $W(R)$ may be related to the density fluctuations as follows [4], [5]. Denoting by z_i and z_k the numbers of particles contained in infinitely small volume elements dv_i, dv_k located at distance R_{ik} from each other, we have, since the probability that the numbers z_i and z_k take values other than zero or one is negligible:

$$\left\{ \begin{aligned} (z_i^2)_{Av} &= (z_i)_{Av} = \rho \, d v_i , \\ (z_i z_k)_{Av} &= \rho^2 W(R_{ik}) \, d v_i d v_k . \end{aligned} \right. \tag{2}$$

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* *Added in proof:* Practically all the expressions for the correlation function $W(R)$ given in the present paper have already been obtained in a paper by F. London [8] which had escaped my attention. London's results have recently been rederived by G. Leibfried [9]. The only result concerning $W(R)$ which goes essentially beyond the contents of these papers is its asymptotic form (36).

We now consider a volume of linear dimensions larger than the distance R_0 at which $W(R_0)$ may be put equal to one. Denoting by $N = \sum_i z_i$ the number of particles in this volume, we have for its mean square fluctuation:

$$(3)\quad (N^2)_{Av} - (N_{Av})^2 = \sum_i \{ (z_i^2)_{Av} - (z_i)^2_{Av} \} + \sum_{i,k}{}' (z_i z_k)_{Av} - (z_i)_{Av} (z_k)_{Av} .$$

Introducing (2) into (3), we find

$$(4)\qquad 1 + \rho \int \{ W(R) - 1 \} d\bar{R} = \frac{(N^2)_{Av} - (N_{Av})^2}{N_{Av}} .$$

The mean square fluctuation of N and hence the left hand side of (4) may be expressed in terms of the compressibility.

We finally shall need the following relation between the scattering cross section and $W(R)$:

$$(5)\qquad \sigma(h) = 1 + \rho \int \{ W(R) - 1 \} e^{2\pi i \bar{h} \bar{R}} d\bar{R} .$$

Here $\sigma(h)$ is the scattering cross section per particle per unit solid angle in units of the scattering cross section per unit solid angle of the isolated particle. $2\pi\bar{h}$ is the difference of the wave vectors of incoming and scattered wave, h is related to the scattering angle θ by

$$(6)\qquad h = \frac{2 \sin \frac{\theta}{2}}{\lambda}$$

where λ is the wave length. The first term in (5) represents the scattering by the isolated particle, the second term the interference effect. According to (5) $\frac{\sigma(h) - 1}{\rho}$ is the three dimensional Fourier transform of $W(R) - 1$. For the scattering cross section in the forward direction ($h = 0$) we have from (5) and (4)

$$(5a)\qquad \sigma(0) = \frac{(N^2)_{Av} - (N_{Av})^2}{N_{Av}} .$$

Eq. (5) has first been derived by Zernike and Prins [5] on the basis of classical interference theory for the particular case of scattering of X-rays by liquids. It describes correctly the scattering of light or particles by a quantum gas without interaction if the deviation of the refractive index of the gas from unity is very small compared to unity and if furthermore the change of the energy of the incident light quantum or particle in the scattering process is negligible. For systems of interacting particles the conditions for the validity of (5) are far more stringent, but do not concern us here.

3. Determination of $W(R)$ and $\sigma(h)$

We now proceed to the calculation of the pair density $\rho_2(\bar{r}, \bar{r}')$ for a system of noninteracting particles. If the particles have a spin, s, we have to distinguish $2s + 1$ spin directions. Since particles of different spin directions are independent we need only to calculate the pair density for particles of parallel spin. This may be done by considering only particles of one spin direction and paying no further attention to the spin. All quantities used in the following will thus refer to particles of one spin direction. Only for the ordinary density will this be explicitly indicated by a subscript 0.

We consider a system of Z noninteracting particles enclosed in a volume V. Denoting the eigenfunction of an individual particle in the quantum state "a" by $\psi_a(\bar{r})$, the probability $\rho_a(\bar{r})d\bar{r}$ of finding a particle which is in state a, in the volume element $d\bar{r}$ is

$$\rho_a(\bar{r})\,d\bar{r} = |\psi_a(\bar{r})|^2 d\bar{r}, \qquad \int |\psi_a(\bar{r})|^2 d\bar{r} = 1 .$$

We have thus for the density $\rho_0(\bar{r})$:

$$\rho_0(\bar{r}) = \sum_a \bar{n}_a \rho_a(\bar{r}) = \sum_a \bar{n}_a |\psi_a(\bar{r})|^2 \tag{7}$$

where $\bar{n}_a$ is the average number of particles in the state "a" and

$$\sum n_a = Z .$$

If we were to pay no attention to the symmetry condition to be imposed on the total wave function of the system, the pair density would be given by

$$\begin{aligned}\rho_2(\bar{r}, \bar{r}') &= \sum_{a,b}{}' \overline{n_a n_b}\, \rho_a(\bar{r})\, \rho_b(\bar{r}') + \sum_a \overline{n_a(n_a-1)}\, \rho_a(\bar{r})\, \rho_a(\bar{r}') \\ &= \sum_{a,b}{}' \overline{n_a n_b}\, |\psi_a(\bar{r})\psi_b(\bar{r}')|^2 + \sum_a \overline{n_a(n_a-1)}\, |\psi_a(\bar{r})\psi_a(\bar{r}')|^2 .\end{aligned}$$

For Bose-Einstein statistics (symmetric wave function) we have to replace the product $\psi_a(\bar{r})\psi_b(\bar{r}')$ by $\frac{1}{\sqrt{2}}\{\psi_a(\bar{r})\psi_b(\bar{r}') + \psi_a(\bar{r}')\psi_b(\bar{r})\}$ for $a \neq b$ (first sum) while the second sum remains unchanged. For Fermi-Dirac statistics (antisymmetric wave function) the second sum has to be omitted while in the first sum $\psi_a(\bar{r})\psi_b(\bar{r}')$ is replaced by $\frac{1}{\sqrt{2}}\{\psi_a(\bar{r})\psi_b(\bar{r}') - \psi_a(\bar{r}')\psi_b(\bar{r})\}$.

We have thus

$$\rho_2(\bar{r}, \bar{r}') = \frac{1}{2}\sum_{a,b}{}' \overline{n_a n_b}\, |\psi_a(\bar{r})\psi_b(\bar{r}') \pm \psi_a(\bar{r}')\psi_b(\bar{r})|^2 + \begin{cases} \overline{n_a(n_a-1)}\, |\psi_a(\bar{r})\psi_a(\bar{r}')|^2 \\ 0 \end{cases}, \tag{8}$$

where the upper and lower lines have to be taken for Bose-Einstein and Fermi-Dirac statistics, respectively. With the relation [6]

$$\overline{n_a n_b} = \bar{n}_a \bar{n}_b, \qquad \overline{n_a(n_a-1)} = \begin{cases} 2(\bar{n}_a)^2 \\ 0 \end{cases}, \tag{8a}$$

(8) may be written

$$\rho_2(\bar{r}, \bar{r}') = \frac{1}{2}\sum_{a,b} \bar{n}_a \bar{n}_b\, |\psi_a(\bar{r})\psi_b(\bar{r}') \pm \psi_a(\bar{r}')\psi_b(\bar{r})|^2 . \tag{8b}$$

Resolving the absolute square in (8b) and using (7), we obtain

$$\rho_2(\bar{r}, \bar{r}') = \rho_0(\bar{r})\,\rho_0(\bar{r}') \pm \Big| \sum_a \bar{n}_a \psi_a^*(\bar{r})\,\psi_a(\bar{r}') \Big|^2 . \tag{9}$$

We now specialize (9) to the case of a gas without external forces. Here the eigenfunctions are plane waves

$$\psi_a(\bar{r}) = \frac{e^{2\pi i \bar{k}_a \cdot \bar{r}}}{\sqrt{V}} \tag{10}$$

and the density $\rho_0(\bar{r})$ is independent of $\bar{r}$:

$$\rho_0 = \frac{\sum_a n_a}{V} = \frac{Z}{V} . \tag{11}$$

The average number of particles in state "*a*" is given [6] by

$$\bar{n}_a = \frac{1}{B e^{\pi k_a^2/k_t^2} \mp 1} \tag{12}$$

with

$$k_t = \sqrt{\frac{2\pi m\,\kappa T}{h^2}} \tag{13}$$

(*m* mass, *κ* Boltzmann's constant, *T* temperature, *h* Planck's constant). The upper and lower signs in (12) have to be taken for Bose-Einstein and Fermi-Dirac statistics, respectively. *B* is a normalizing constant determined by (11).

The number of states in a small interval $\Delta\bar{k}$ is given by $V\Delta\bar{k}$. Introducing now (10) and (12) into the sums in (9) and (11), and replacing the sums by integrals, we have, with

$$n(k) = \frac{1}{B e^{\pi k^2/k_t^2} \mp 1} , \tag{14}$$

$$\rho_0 = \int n(k)\, d\bar{k} , \tag{15}$$

$$\sum_a \bar{n}_a \psi_a(\bar{r})\,\psi_a^*(\bar{r}') = \int n(k)\, e^{2\pi i \bar{k}\cdot(\bar{r}-\bar{r}')} d\bar{k} , \tag{16}$$

and thus

$$\rho_2(\bar{r}, \bar{r}') = \rho_0 \pm \Big(\int n(k)\, e^{2\pi i \bar{k}\cdot(\bar{r}-\bar{r}')} d\bar{k} \Big)^2 . \tag{17}$$

Since $n(k)$ depends only on the magnitude of *k*, its Fourier transform and hence the pair density depends only on $R = |\bar{r} - \bar{r}'|$. From (17) and (1) we have finally

$$W_0(R) = 1 \pm \Big(\frac{\tilde{n}(R)}{\rho_0} \Big)^2 \tag{18}$$

where the index 0 on *W* indicates that in the case of particles with spin it refers to particles of parallel spin only. $\tilde{n}(R)$ stands for the Fourier transform of $n(k)$,

$$\tilde{n}(R) = \int n(k)\, e^{2\pi i\bar{k}.\bar{R}} d\bar{k} = \int \frac{e^{2\pi i\bar{k}.\bar{R}}}{Be^{\pi k^2/k_t} \mp 1}\, d\bar{k} \tag{19}$$

$$= \frac{1}{2R} \int_0^\infty \frac{\sin 2\pi kR}{Be^{\pi k^2/k_t^2} \mp 1}\, k\,dk\,.$$

For particles of spin s we have

$$\rho = (2s+1)\,\rho_0\,, \tag{20}$$

$$W(R) = \frac{1}{2s+1}\,\{2s + W_0(R)\} = 1 + \frac{W_0(R) - 1}{2s+1}\,, \tag{21}$$

and

$$W(R) - 1 = \frac{1}{2s+1}\,\{W_0(R) - 1\} = \pm \frac{1}{2s+1}\left(\frac{\tilde{n}(R)}{\rho_0}\right)^2. \tag{18a}$$

Noting that, from (12)

$$\tilde{n}(0) = \rho_0 \tag{22}$$

we have, for $R = 0$

$$W_0(0) = \begin{cases} 2 \text{ for B.E. statistics} \\ 0 \text{ for F.D. statistics} \end{cases} \tag{23}$$

and

$$W(0) = 1 \pm \frac{1}{2s+1}\,. \tag{24}$$

From (5), (20) and (18a) we have for the cross section

$$\sigma(h) = 1 + \rho \int [W(R) - 1]\, e^{2\pi i\bar{h}.\bar{R}} d\bar{R}$$

$$= 1 + \rho_0 \int [W_0(R) - 1]\, e^{2\pi i\bar{h}.\bar{R}} d\bar{R} = 1 + \frac{1}{\rho_0} \int [\tilde{n}(R)]^2 e^{2\pi i\bar{h}.\bar{R}} d\bar{R}$$

and, using the convolution theorem,

$$\sigma(h) = 1 \pm \frac{1}{\rho_0} \int n(k)\, n(|\bar{k} + \bar{h}|)\, d\bar{k}\,. \tag{25}$$

From (25) and (5a) we obtain for the mean square density fluctuation

$$\frac{(N^2)_{Av} - (N_{Av})^2}{N_{Av}} = \sigma(0) = 1 \pm \frac{1}{\rho_0} \int n^2(k)\, dk\,. \tag{26}$$

4. Degenerate Fermi gas

For a fully degenerate Fermi gas

$$n(k) = \begin{cases} 1 \text{ for } k < k_0 \\ 0 \text{ for } k > k_0 \end{cases} \tag{27}$$

where, from (14),

$$k_0 = \left(\frac{3}{4\pi}\right)^{1/3} \rho_0^{1/3}\,. \tag{28}$$

$\tilde{n}(R)$ is thus here the Fourier transform of the step function. From (19) we have immediately

$$\frac{\tilde{n}(R)}{\tilde{n}(0)} = \frac{3}{x^2}\left\{\frac{\sin x}{x} - \cos x\right\} = 3\sqrt{\frac{\pi}{2}}\,\frac{J_{3/2}(x)}{x^{3/2}}\,, \tag{29}$$

where

$$x = 2\pi k_0 R = (6\pi^2)^{1/3}\rho_0^{1/3}R \tag{29a}$$

so that

$$W_0(R) = 1 - \frac{9\pi}{2}\,\frac{[J_{3/2}(x)]^2}{x^3} \tag{30}$$

and, for $s = \frac{1}{2}$

$$W(R) = 1 - \frac{9\pi}{4}\,\frac{[J_{3/2}(x)]^2}{x^3}\,. \tag{31}$$

(30) has been obtained by Wigner and Seitz [2] in a somewhat different way.

Figure 1 shows the functions $W_0(R)$ and $W(R)$. For all R we have $W_0(R) \leqq 1$;

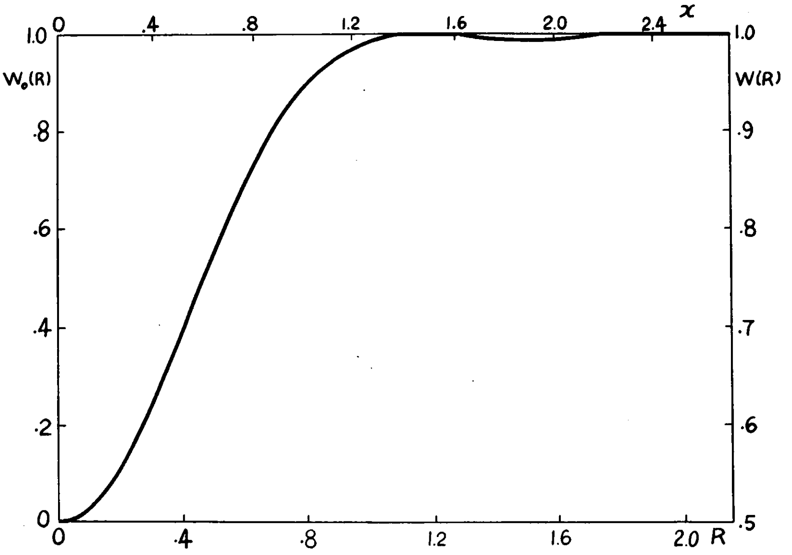

FIGURE 1

The functions $W_0(R)$ and $W(R)$

at all its maxima the function $W_0(R)$ has the value 1, its minima [except of course the first one, $W(0) = 0$] are very little pronounced.

For the cross section one obtains from (27) and (25)

$$\sigma(h) = \begin{cases} \frac{3}{2}y\left(1 - \frac{1}{3}y^2\right) & \text{for } y < 1\,, \\ 1 & \text{for } y > 1\,, \end{cases} \qquad y = \frac{h}{2k_0} = \left(\frac{\pi^2}{6}\right)^{1/3}\frac{h}{\rho_0^{1/3}} = \left(\frac{\pi^2}{3}\right)^{1/3}\frac{h}{\rho^{1/3}}\,. \tag{32}$$

The correlation diminishes thus the scattering for small h, while for $h > 2k_0$ there is no correlation effect. This may also be understood by momentum considerations.

If the momentum transferred to a particle in the scattering process is smaller than twice the maximum momentum of the particles, some of the transitions will lead to occupied states and are thus excluded by the Pauli principle.

5. Other cases

In the limit of zero density B goes to infinity and

$$\frac{n(k)}{\rho_0} = k_t^3 e^{-\pi k^2/k_t^2}.$$

Hence

$$\frac{\tilde{n}(R)}{\rho_0} = e^{-\pi (k_t R)^2}$$

and

$$W(R) = 1 \pm \frac{e^{-2\pi (k_t R)^2}}{2s+1}. \tag{33}$$

Except for the spin factor, (33) agrees with the expression given by De Boer [1] for this case.

For $B > 1$, $n(k)$ may be expanded in inverse powers of B

$$n(k) = \sum_{m=1}^{\infty} (\pm 1)^{m-1} e^{-m\pi k^2/k_t^2} B^{-n}$$

and hence we have for $\tilde{n}(R)$:

$$\tilde{n}(R) = k_t^3 \sum_{m=1}^{\infty} (\pm 1)^{m-1} \frac{e^{-\pi (k_t R)^2/m}}{m^{3/2}} B^{-m} \tag{34}$$

where B is determined by

$$\rho_0 = \tilde{n}(0) = k_t^3 \sum_{m=1}^{\infty} \frac{(\pm 1)^{m-1}}{m^{3/2}} B^{-m}. \tag{35}$$

Determining B as a function of ρ_0/k_t^3 from (35) and introducing it into (34), one obtains $W(R)$ from (18a). For $B - 1 << 1$ the expansion (34) is impractical. In this case one has to return to the original integral (19). For the Bose gas one obtains by contour integration

$$W(R) - 1 = \frac{.146\, e^{-R/L}}{(2s+1)(k_t R)^2}, \qquad B - 1 << 1, \qquad k_t R >> 1, \tag{36}$$

where the correlation length L is defined by

$$k_t L = \frac{1}{4\sqrt{\pi}\,(B-1)} = .135 \frac{\rho_c}{\rho - \rho_c}. \tag{36a}$$

ρ_c is the condensation density given by (35) for $B = 1$, [7], namely,

$$\rho_c = k_t^3 \zeta(\tfrac{3}{2}).$$

(36a) shows the increase of the correlation length on the approach to condensation.

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