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Quantum corrections to the radial distribution function of a fluid

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Explicit expressions for the first quantum correction to the radial distribution function of a fluid were given by several authors, either in terms of canonical classical distribution functions [1, 2] or in terms of grand-canonical classical distribution functions [3]. These expressions are rather complicated and contain classical distribution functions up to the five-particle one. In the present note we give a much simpler equivalent expression which contains the classical distribution functions only up to the four-particle one. In the special case of the one-component plasma, further simplifications occur, and the first quantum correction to the radial distribution function can be expressed in terms of the sole classical radial distribution function. We use the notation of Gibson [3].

To first-order in $\hbar^2$, the Wigner–Kirkwood expansion of the N-particle Boltzmann factor is [4], in terms of the total potential energy U,

$$\exp(-\beta U)\left[1+\frac{\hbar^2\beta^3}{24m}\sum_i(\nabla_i U)^2-\frac{\hbar^2\beta^2}{12m}\sum_i\nabla_i{}^2U\right]$$

$$=\exp(-\beta U)\left[1-\frac{\hbar^2\beta^2}{24m}\sum_i\nabla_i{}^2U\right]+\frac{\hbar^2\beta}{24m}\sum_i\nabla_i{}^2\exp(-\beta U). \qquad (1)$$

When integrated over the coordinates of particle i, the term $\nabla_i{}^2\exp(-\beta U)$ gives no volume contribution. Therefore, the quantum radial distribution function is

$$g^{\mathrm{q}}(12)=\frac{\begin{aligned}N(N-1)\int\Big[\exp(-\beta U)\left(1-\frac{\hbar^2\beta^2}{24m}\sum_i\nabla_i{}^2U\right)+\frac{\hbar^2\beta}{24m}\\ \times(\nabla_1{}^2+\nabla_2{}^2)\exp(-\beta U)\Big]\,d3\ldots dN\end{aligned}}{\rho^2\int\exp(-\beta U)\left(1-\frac{\hbar^2\beta^2}{24m}\sum_i\nabla_i{}^2U\right)d1\ldots dN}. \qquad (2)$$

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Equivalently, to first order in $\hbar^2$,

$$g^{q}(12)=\frac{N(N-1)\int\left[\exp(-\beta U)\left(1-\frac{\hbar^2\beta^2}{24m}\sum_i\nabla_i^2U\right)+\frac{\hbar^2\beta}{24m}\times(\nabla_1^2+\nabla_2^2)\exp(-\beta U)\right]d3\ldots dN}{\rho^2\int\exp(-\beta U)\,d1\ldots dN}$$
$$+\frac{N(N-1)\int\exp(-\beta U)d3\ldots dN\int\exp(-\beta U)\frac{\hbar^2\beta^2\rho^2}{24m}\times\left(\sum_i\nabla_i^2U\right)d1\ldots dN}{\left[\rho^2\int\exp(-\beta U)\,d1\ldots dN\right]^2}. \tag{3}$$

If U is a sum of pair potentials u_{ij},

$$\nabla_i^2U=\sum_{\substack{j\\ j\neq i}}\nabla_i^2u_{ij}, \tag{4}$$

and grouping equivalent terms in (3) gives the result

$$g^{q}(12)=g^{c}(12)\left[1-\frac{\hbar^2\beta^2}{12m}\nabla^2{}_1u_{12}\right]+\frac{\hbar^2\beta}{12m}\nabla_1^2g^{c}(12)$$
$$-\frac{\hbar^2\beta^2\rho}{6m}\int g^{c}(123)\nabla_1^2u_{13}\,d3$$
$$+\frac{\hbar^2\beta^2\rho^2}{24m}\int\left[g^{c}(12)g^{c}(34)-g^{c}(1234)\right]\nabla_3^2u_{34}\,d3\,d4, \tag{5}$$

where the g^{c} are canonical classical distribution functions. As pointed out by Gibson [3], it is more convenient for practical purposes to use grand-canonical classical distribution functions; when using such grand-canonical functions, for which we keep the same notation g^{c}, one must add to (5)

$$\frac{\hbar^2\beta}{24m}\frac{1}{\rho}\left(\frac{\partial\rho}{\partial p_0}\right)\frac{\partial}{\partial\rho}\left[\rho^2g^{c}(12)\right]\int\frac{\partial}{\partial\rho}\left[\rho^2g^{c}(34)\right]\nabla_3^2u_{34}\,d4. \tag{6}$$

It can be verified that Gibson's equation (17) of [3] does simplify to our form (5), (6) by integrations by parts and use of the equations of the BGY hierarchy.

In the special case of a one-component plasma (particles of charge e neutralized by a uniform charged background), (4) is to be replaced by

$$\nabla_i^2U=-4\pi e^2\sum_{\substack{j\\ j\neq i}}\delta(r_{ij})+4\pi e^2\rho. \tag{7}$$

In (3), the contributions of the background term $4\pi e^2\rho$ of (7) cancel one another. The δ terms of (7) do not give any contributions since they are weighted by classical Boltzmann factors which vanish at zero interparticle distance. Therefore, (5) reduces to the very simple result

$$g^{q}(r)=g^{c}(r)+\frac{\hbar^2\beta}{12m}\nabla^2g^{c}(r). \tag{8}$$

Unfortunately (8) cannot be used for too small values of r, however high the temperature may be. For small values of r, g^c is proportional to $\exp(-\beta e^2/r)$ and (8) becomes

$$g^q(r) \approx \left[1 + \frac{\hbar^2 \beta^3 e^4}{12mr^4} \right] g^c(r) \, ; \qquad (9)$$

for too small values of r, the second term in the bracket of (9) is no longer a quantum 'correction', and the whole Wigner–Kirkwood expansion scheme breaks down [5].

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