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# First Order Perturbation Calculation for the Dynamical Correlation Function of a Classical Gas

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*Abstract.* For a classical gas with a finite twobody potential the dynamical correlation function has been evaluated to first order in the interaction. An extrapolation of this result is discussed for gases with more realistic interactions.

*Zusammenfassung.* Für ein klassisches Gas von identischen Teilchen, ohne innere Struktur, welche durch ein beschränktes Zweikörper-Potential wechselwirken, wird die dynamische Korrelationsfunktion in erster Ordnung der Kopplungskonstante berechnet. Das Resultat wird auf Gase mit einer realistischeren Wechselwirkung extrapoliert.

## 1. Introduction

In the theory of real gases and liquids various approximations and expansions for the static two-particle correlation [1, 2] have been given. Recently several approaches to a theory of the dynamical correlation have been discussed [1], [3–7]. The present paper proposes a perturbation expansion of the dynamical correlation function and evaluates the term linear in the interaction.

We consider a classical gas of identical particles without internal structure. We assume that the interaction between the particles is given by a finite two-body potential.

The dynamical correlation function for such a system is defined as:

$$G(r, t) = G_d(r, t) + G_s(r, t) ,$$

$$\varrho\, G_d(r, t) = \frac{1}{N} \langle \sum_{i \neq j} \delta\big(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)\big)\rangle \tag{1.1}$$

$$\varrho\, G_s(r, t) = \langle \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)\rangle .$$

Here $\langle \cdots \rangle$ is the canonical statistical average in the thermodynamic limit. $N$ is the number of particles in the system, $\mathbf{r}_j(t)$ the position of the particle $j$ at time $t$ and $\varrho$ the particle density. The function $G_d(r, t)$ is the distinct part and $G_s(r, t)$ the self part of the dynamical correlation function.

The intermediate scattering function is defined by:

$$I(q, t) = \varrho \int d^3r\, e^{iqr} \, [G(r, t) - 1] \, . \tag{1.2}$$

Therefore

$$I(q, t) = \frac{1}{N} \langle \varrho(-\boldsymbol{q}, 0) \, \varrho(\boldsymbol{q}, t) \rangle - 2 \pi \varrho \, \delta(\boldsymbol{q}) \tag{1.3}$$

with

$$\varrho \, (\boldsymbol{q}, t) = \sum_{i=1}^{N} e^{i\boldsymbol{q}\boldsymbol{r}_i(t)} \, .$$

The Fourier transformed of $I(q, t)$ with respect to time is $S(q, \omega)$:

$$I(q, t) = \int_{-\infty}^{\infty} d\omega \, e^{i\omega t} \, S(q, \omega) \, . \tag{1.4}$$

The development of $I(q, t)$ with respect to time:

$$I(q, t) = \sum_{n=0}^{\infty} \Omega_{2n}(q) \, \frac{(i\, t)^{2n}}{(2\, n)!} \tag{1.5}$$

involves the $(2\, n)$th moment of $S(q, \omega)$:

$$\Omega_{2n}(q) = \int_{-\infty}^{\infty} d\omega \, S(q, \omega) \, \omega^{2n} \, .$$

For a classical gas the odd moments vanish, since $S(q, \omega) = S(q, -\omega)$ [1].

For $n > 0$ the equations (1.3) and (1.5) together with the stationarity condition (see e.g. [8], pag. 154) lead to:

$$\Omega_{2n}(q) = \frac{1}{N} \left\langle \left| \frac{d^n}{dt^n} \varrho(\boldsymbol{q}, t) \right|^2 \right\rangle \Bigg|_{t=0} \, .$$

The moments can be calculated with this equation in terms of the potential and the static correlation functions:

$$\varrho^s \, g_s(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_s) = \frac{1}{Q_N} \frac{N!}{(N - S)!} \int d^3r_{s+1} \ldots d^3r_N \, e^{-\beta H_1} \, , \tag{1.6}$$

where

$$Q_N = \int d^3r_1 \ldots d^3r_N \, e^{-\beta H_1} \, , \quad \beta = \frac{1}{k\, T}$$

and where $H_1$ is the potential energy. Thus $\Omega_2$ and $\Omega_4$ have been calculated in [1] and $\Omega_6$ in [9]. Appendix II gives the expression for $\Omega_8$. The rather cumbersome derivation of this result has been omitted. Note that the expression for $\Omega_8$ contains correlations up to four particles, which are not readily known.

In the following we shall assume that the interaction potential between the particles $U(r) \equiv \lambda\, u(r)$ has the properties:

a) $U(r) \in L_1(R_3)$ and $\lim_{r \to \infty} U(r) = 0$.

b) In the interval $0 \leq r < \infty$ the first derivative of $U(r)$ exists. This implies that $U(r)$ is finite. Actually it turns out that the result depends on the potential and not on its derivatives, so possibly only the finiteness of $U(r)$ is essential.

We further assume that for sufficiently small $\lambda\beta$ the dynamical correlation has the expansion:

$$G(\lambda\beta, r, t) = G^0(r, t) + \lambda\beta\, G^1(r, t) + O\big((\lambda\beta)^2\big)$$

and that:

$$I(\lambda\beta, q, t) = I^0(q, t) + \lambda\beta\, I^1(q, t) + O\big((\lambda\beta)^2\big)$$

and similarly for $S(\lambda\beta, q, \omega)$.

Obviously $G^0(r, t)$ is the dynamical correlation function of the ideal gas. The purpose of this work is to compute the first order correction, i.e. $\lambda\beta\, G^1(r, t)$, as well as its Fourier transformed $\lambda\beta\, S^1(q, \omega)$. This will be done in Section 2. Section 3 discusses possible extrapolations of the result. In Appendix I we also calculate $\lambda\beta\, I^1(q, t)$.

## 2. The First Order Correction

We shall now calculate $\lambda\beta\, G^1(r, t)$. It is convenient to consider first $\lambda\beta\, I^1(q, t)$ i.e. the first order contribution to:

$$I(q, t) = \frac{1}{Z_N\, N} \int e^{-\beta H}\, \varrho(-\boldsymbol{q}, 0)\, \varrho(\boldsymbol{q}, t)\, d\Omega - 2\pi\varrho\, \delta(\boldsymbol{q})$$

with $d\Omega$ the volume element of the phase space and

$$Z_N = \int e^{-\beta H}\, d\Omega\,.$$

The Hamiltonian of the system is:

$$H = H_0 + H_1\,,$$

where

$$H_0 = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m}$$

is the kinetic energy and

$$H_1 = \frac{1}{2} \sum_{k \neq l} U(|\, \boldsymbol{r}_k - \boldsymbol{r}_l \,|)$$

the potential energy. The Liouville operator $L$ is given by:

$$L = \sum_{k=1}^{N} \left( \frac{\partial H}{\partial \boldsymbol{p}_k} \frac{\partial}{\partial \boldsymbol{r}_k} - \frac{\partial H}{\partial \boldsymbol{r}_k} \frac{\partial}{\partial \boldsymbol{p}_k} \right) = \{H,.\} ,$$

where $\{\,.\,,\,.\,\}$ is the Poisson bracket. Thus if $h(x)$ is a function of the coordinates of the system at time $t$:

$$h\big(x(t)\big) = e^{Lt}\, h\big(x(0)\big) .$$

Let $L_0$ be the Liouville operator to the unperturbed Hamiltonian $H_0$. Then

$$I(q, t) = \frac{1}{Z_N N} \int e^{-\beta H} \varrho(- \boldsymbol{q}, 0)\, e^{Lt} \varrho(\boldsymbol{q}, 0)\, d\Omega - 2 \pi \varrho\, \delta(\boldsymbol{q})$$

$$= \frac{1}{Z_N N} \int e^{-L_0 t} [e^{-\beta H} \varrho(- \boldsymbol{q}, 0)\, e^{Lt} \varrho(\boldsymbol{q}, 0)]\, d\Omega - 2 \pi \varrho\, \delta(\boldsymbol{q})$$

$$= \frac{1}{Z_N N} \int e^{-\beta H_0}\, e^{-\beta \widehat{H}_1(t)}\, \widehat{\varrho}(- \boldsymbol{q}, t)\, [e^{-L_0 t} e^{Lt} \varrho(\boldsymbol{q}, 0)]\, d\Omega - 2 \pi \varrho\, \delta(\boldsymbol{q}) , \quad (2.1)$$

where

$$\widehat{h}\big(x(t)\big) = e^{-L_0 t}\, h\big(x(0)\big) .$$

From:

$$\frac{\partial}{\partial t} [e^{-L_0 t} e^{Lt}] = e^{-L_0 t} (L - L_0)\, e^{Lt}$$

follows

$$\frac{\partial}{\partial t} [e^{-L_0 t} e^{Lt} \varrho(\boldsymbol{q}, 0)] = e^{-L_0 t} \{H_1, e^{Lt} \varrho(\boldsymbol{q}, 0)\} .$$

Thus the partial differential equation holds:

$$\frac{\partial}{\partial t} [e^{L_0 t} e^{Lt} \varrho(\boldsymbol{q}, 0)] = \{\widehat{H}_1(t), e^{-L_0 t} e^{Lt} \varrho(\boldsymbol{q}, 0)\} .$$

The solution is:

$$e^{-L_0 t} e^{Lt} \varrho(\boldsymbol{q}, 0) = \varrho(\boldsymbol{q}, 0) + \int_0^t dt_1 \{\widehat{H}_1(t_1), \varrho(\boldsymbol{q}, 0)\}$$

$$+ \int_0^t dt_1 \int_0^{t_1} dt_2 \{\widehat{H}_1(t_1), \{\widehat{H}_1(t_2), \varrho(\boldsymbol{q}, 0)\}\} + \cdots \quad (2.2)$$

as can be verified by partial differentiation with respect to $t$.

The first order contributions to $I(q, t)$ arise from the first two terms of this series. The term $\varrho(\boldsymbol{q}, 0)$ substituted into (2.1) leads to an expression which we designate by $A$.

We introduce the symbol $\stackrel{1}{=}$:
$a \stackrel{1}{=} b$ states that the first order term with respect to $\lambda$ in $a$ equals that in $b$.
With this convention:

$$A \stackrel{1}{=} \frac{1}{Z_N N} \int e^{-\beta H_0} e^{-\beta \hat{H}_1(t)} \hat{\varrho}(-\boldsymbol{q}, t)\, \varrho(\boldsymbol{q}, 0)\, d\Omega$$

$$= \frac{1}{Z_N N} \int e^{-\beta H} \varrho(-\boldsymbol{q}, 0)\, e^{L_0 t} \varrho(\boldsymbol{q}, 0)\, d\Omega$$

$$= \frac{1}{Z_N N} \sum_{i,j} \int e^{-\beta H} e^{-i\boldsymbol{q}\boldsymbol{r}_i} e^{i[\boldsymbol{q}, \boldsymbol{r}_j + (t/m)\boldsymbol{p}_j]}\, d\Omega .$$

For $i = j$ the integral over configuration space cancels with the corresponding factor in $Z_N$. In $A$ therefore only terms with $i \neq j$ contribute to the first order. Hence with the definition (1.6) and $\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$:

$$A \stackrel{1}{=} \frac{(N-1)}{Z_N} \int e^{-\beta H} e^{i(\boldsymbol{q}, \boldsymbol{r}_1 - \boldsymbol{r}_2)} e^{i(t/m)\boldsymbol{q}\boldsymbol{p}_1}\, d\Omega$$

$$= \left(\frac{2\pi m}{\beta}\right)^{-3/2} \varrho \int g_2(r)\, e^{i\boldsymbol{q}\boldsymbol{r}}\, d^3r \int e^{-(\beta/2m)p_1^2} e^{i(t/m)\boldsymbol{q}\boldsymbol{p}_1}\, d^3p_1 .$$

Now (see e.g. [2], pag. 64):

$$g_2(r) = 1 - \lambda\beta\, u(r) + O((\lambda\beta)^2),$$

so that

$$A \stackrel{1}{=} -\varrho\beta\, \tilde{U}(q)\, e^{-(q^2/2m\beta)t^2}, \tag{2.3}$$

where $\tilde{U}(q)$ is the three dimensional Fourier transformed of the potential $U(r) = \lambda\, u(r)$.
Let us now consider the second term of series (2.2):

$$\int_0^t dt_1 \{\hat{H}_1(t_1), \varrho(\boldsymbol{q}, 0)\} = \int_0^t dt_1 \sum_{k=1}^{N} \frac{\partial \hat{H}_1(t_1)}{\partial \boldsymbol{p}_k} \frac{\partial}{\partial \boldsymbol{r}_k} e^{i\boldsymbol{q}\boldsymbol{r}_k}$$

$$= \int_0^t dt_1 \sum_{k \neq l} e^{i\boldsymbol{q}\boldsymbol{r}_k} \left(-i\frac{t_1}{m}\right) (\boldsymbol{q}, \operatorname{grad} \hat{U}_{kl}(t_1))$$

with

$$\hat{U}_{kl}(t_1) = U\left(\boldsymbol{r}_k - \boldsymbol{r}_l - \frac{t_1}{m}(\boldsymbol{p}_k - \boldsymbol{p}_l)\right).$$

Inserted into (2.1) this term leads to an expression $B$:

$$B \stackrel{1}{=} \left(\frac{2\pi m}{\beta}\right)^{-(3N/2)} \frac{1}{N} \sum_{i=1}^{N} \sum_{k \neq l} \int_0^t dt_1 \int d\Omega\, e^{-\beta H_0} e^{i(\boldsymbol{q}, \boldsymbol{r}_k - \boldsymbol{r}_i)}$$

$$\times\, e^{i(t/m)\boldsymbol{q}\boldsymbol{p}_i} \left(-i\frac{t_1}{m}\right) (\boldsymbol{q}, \operatorname{grad} \hat{U}_{kl}(t_1)) .$$

Since $U(r)$ vanishes at infinity, only the terms with $i = l$ differ from zero. Thus the linear terms of both $A$ and $B$ belong to $G_d(r, t)$. From the evaluation:

$$B \stackrel{1}{=} \frac{(N-1)}{V^N} \left(\frac{2\pi m}{\beta}\right)^{-(3N/2)} \int_0^t dt_1 \int d\Omega \, e^{-\beta H_0} \, e^{i(\boldsymbol{q}, \boldsymbol{r}_1 - \boldsymbol{r}_2)}$$

$$\times \, e^{i(t/m)\boldsymbol{q}\boldsymbol{p}_2} \left(-i \frac{t_1}{m}\right) (\boldsymbol{q}, \operatorname{grad} \widehat{U}_{12}(t_1))$$

$$= \varrho \left(\frac{\beta}{2\pi m}\right)^3 \int_0^t dt_1 \int d^3p_1 \, d^3p_2 \, e^{-(\beta/2m)(p_1^2 + p_2^2)} \int d^3r \, e^{i\boldsymbol{q}\boldsymbol{r}}$$

$$\times \, e^{i(t/m)\boldsymbol{q}\boldsymbol{p}_2} \left(-i \frac{t_1}{m}\right) \left(\boldsymbol{q}, \operatorname{grad} U\left(\boldsymbol{r} - \frac{t_1}{m}(\boldsymbol{p}_1 - \boldsymbol{p}_2)\right)\right).$$

We put

$$\zeta = \boldsymbol{r} - \frac{t_1}{m}(\boldsymbol{p}_1 - \boldsymbol{p}_2)$$

and after partial integration:

$$B \stackrel{1}{=} -\varrho \, q^2 \, \tilde{U}(q) \left(\frac{\beta}{2\pi m}\right)^3 \int_0^t dt_1 \int d^3p_1 \, d^3p_2 \, e^{-(\beta/2m)(p_1^2 + p_2^2)}$$

$$\times \, e^{i(t_1/m)(\boldsymbol{q}, \boldsymbol{p}_1 - \boldsymbol{p}_2)} \, e^{i(t/m)\boldsymbol{q}\boldsymbol{p}_2} \frac{t_1}{m}.$$

Integration over momenta gives:

$$B \stackrel{1}{=} -\varrho \, q^2 \frac{\tilde{U}(q)}{m} \int_0^t dt_1 \, t_1 \, e^{-(q^2 t_1^2/2m\beta)} \, e^{-[q^2(t-t_1)^2/2m\beta]}. \tag{2.4}$$

$\lambda \beta I^1(r, t)$ is the sum of the righthand sides of (2.3) and (2.4). It has the form:

$$\lambda \beta I^1(q, t) = -\varrho \beta \tilde{U}(q) \tilde{f}(q, t)$$

$\varrho \lambda \beta G^1(r, t)$, being its three dimensional Fourier transformed, is a Faltung:

$$\lambda \beta G^1(r, t) = -\beta \int d^3r' \, U(r') \, f(|\boldsymbol{r}' - \boldsymbol{r}|, t),$$

where

$$f(r, t) = \frac{1}{(2\pi)^3} \int d^3q \, e^{-i\boldsymbol{q}\boldsymbol{r}} \tilde{f}(q, t).$$

We shall now calculate the function $f(r, t)$. Since it depends on $|\boldsymbol{r}|$ only, it is sufficient to determine the one dimensional Fourier transformed $F(r, t)$:

$$F(r, t) = \frac{1}{2\pi} \int dq \, e^{iqr} \tilde{f}(q, t) ,$$

from which $f(r, t)$ follows through:

$$f(r, t) = -\frac{1}{2\pi} \frac{1}{r} \frac{\partial}{\partial r} F(r, t) . \tag{2.5}$$

$F(r, t)$ separates into the contributions from $A$ and $B$:

$$F(r, t) = F_A(r, t) + F_B(r, t) . \tag{2.6}$$

We easily get:

$$F_A(r, t) = \frac{1}{t} (2\pi m \beta)^{1/2} e^{-(m\beta/2)(r/t)^2} . \tag{2.7}$$

Similarly (2.4) leads to:

$$F_B(r, t) = -\left(\frac{1}{2\pi m \beta}\right)^{1/2} \frac{\partial^2}{\partial r^2} \int_0^t dt_1 \frac{t_1}{[t_1^2 + (t - t_1)^2]^{1/2}} e^{-(m\beta r^2/2)[t_1^2 + (t-t_1)^2]^{-1}} . \tag{2.8}$$

The integral

$$T = \int_0^t dt_1 \frac{t_1}{[t_1^2 + (t - t_1)^2]^{1/2}} e^{-\gamma[t_1^2 + (t-t_1)^2]^{-1}} ,$$

$$\gamma = \frac{m \beta r^2}{2} ,$$

becomes after the substitution:

$$y = t_1 - \frac{t}{2} ,$$

$$T = \int_{-t/2}^{t/2} dy \frac{y}{\left(2y^2 + \frac{t^2}{2}\right)^{1/2}} e^{-\gamma[2y^2 + (t^2/2)]^{-1}} + \frac{t}{2} \int_{-t/2}^{t/2} dy \frac{1}{\left(2y^2 + \frac{t^2}{2}\right)^{1/2}} e^{-\gamma[2y^2 + (t^2/2)]^{-1}} .$$

The first integral vanishes, since the integrand is an odd function. By the transformation:

$$x = 2\left[1 - \frac{t^2}{4}\left(y^2 + \frac{t^2}{4}\right)^{-1}\right] ,$$

the second integral is found to be:

$$T = \frac{t}{4} \int_0^1 dx \frac{1}{x^{1/2}\left(1 - \frac{x}{2}\right)} e^{s(x/2-1)} ,$$

with

$$s = \frac{2\gamma}{t^2} = m\beta \left(\frac{r}{t}\right)^2 . \tag{2.9}$$

For the derivation in (2.8) we note that:

$$\frac{\partial^2}{\partial r^2} = \frac{2 m \beta}{t^2} \frac{\partial}{\partial s} + \left(\frac{2 m \beta}{t^2}\right)^2 r^2 \frac{\partial^2}{\partial s^2} .$$

Developing the exponential in the integrand we get:

$$\frac{\partial}{\partial s} T = -\frac{t}{4} e^{-s} \int_0^1 dx \frac{1}{x^{1/2}} e^{(s/2)x} = -\frac{t}{2} e^{-s}\, {}_1F_1\left(\frac{1}{2}, \frac{3}{2}; \frac{s}{2}\right),$$

where

$${}_1F_1(a, b; z) = 1 + \frac{a}{b} z + \frac{a(a+1)}{b(b+1)} \frac{z^2}{2!} + \cdots$$

is the confluent hypergeometric function. Analogously:

$$\frac{\partial^2}{\partial s^2} T = \frac{t}{2} e^{-s}\, {}_1F_1\left(\frac{1}{2}, \frac{3}{2}; \frac{s}{2}\right) - \frac{t}{4s} e^{-s/2} + \frac{t}{4s} e^{-s}\, {}_1F_1\left(\frac{1}{2}, \frac{3}{2}; \frac{s}{2}\right),$$

so that

$$-\frac{\partial^2}{\partial r^2} T = \frac{1}{t} m\beta e^{-s/2} \left[1 - 2 m\beta \left(\frac{r}{t}\right)^2 e^{-s/2}\, {}_1F_1\left(\frac{1}{2}, \frac{3}{2}; \frac{s}{2}\right)\right] . \tag{2.10}$$

Combining (2.6). (2.7), (2.8), (2.9) and (2.10) we obtain:

$$F(r, t) = \left(\frac{2 m\beta}{\pi}\right)^{1/2} \frac{1}{t} e^{-(m\beta/2)(r/t)^2}$$
$$\times \left[1 - m\beta \left(\frac{r}{t}\right)^2 e^{-(m\beta/2)(r/t)^2}\, {}_1F_1\left(\frac{1}{2}, \frac{3}{2}; \frac{m\beta}{2}\left(\frac{r}{t}\right)^2\right)\right] \tag{2.11}$$

and finally with (2.5):

$$f(r, t) = 2\left(\frac{m\beta}{2\pi}\right)^{3/2} \frac{1}{t^3} e^{-m\beta(r/t)^2}$$
$$\times \left[e^{-(m\beta/2)(r/t)^2} + 2\left(1 - m\beta\left(\frac{r}{t}\right)^2\right) {}_1F_1\left(\frac{1}{2}, \frac{3}{2}; \frac{m\beta}{2}\left(\frac{r}{t}\right)^2\right)\right. \tag{2.12}$$
$$\left. + \frac{m\beta}{3}\left(\frac{r}{t}\right)^2 {}_1F_1\left(\frac{3}{2}, \frac{5}{2}; \frac{m\beta}{2}\left(\frac{r}{t}\right)^2\right)\right] .$$

The function $f(r, t)$ has the following properties:

a) It is normalized

$$\int d^3r\, f(r, t) = 1\,, \tag{2.13}$$

as follows from (2.3), (2.4) and (2.5).

b) Asymptotically for $m\,\beta (r/t)^2 \ll 1$

$$f(r, t) = 6 \left(\frac{m\,\beta}{2\,\pi}\right)^{3/2} \frac{1}{t^3}\,.$$

c) $f(r, 0) = \delta(\mathbf{r})$.

d) For certain ranges of the variables $r$ and $t$ the function $f(r, t)$ is negative as is seen from Figure 1 and (2.5).

For the evaluation of the linear correction to the structure factor:

$$\lambda\,\beta\, S^1(q, \omega) = -\,\varrho\,\beta\,\tilde{U}(q)\,\frac{1}{2\,\pi}\int\limits_{-\infty}^{\infty} dt\, e^{-i\omega t}\,\tilde{f}(q, t)\,,$$

it suffices to note that $f(r, t)$ (see (2.12)) is of the form:

$$f(r, t) = \frac{1}{t^3}\, h\left(\frac{r}{t}\right).$$

From this follows that $\tilde{f}(q, t)$ depends on $q$ and $t$ only through the product $q\,t$. This symmetry implies that the Fourier transformed of $\tilde{f}(q, t)$ with respect time $F(\omega, q)$ is obtained from the function $F(r, t)$ calculated in (2.11) by the substitution $r \to \omega$, $t \to q$, i.e.:

$$\lambda\,\beta\, S^1(q, \omega) = -\,\varrho\,\beta\,\tilde{U}(q)\, F(\omega, q)\,.$$

The function $q(\pi/2\,m\,\beta)^{1/2}\, F(\omega, q) = Z\big((m\,\beta/2)^{1/2}\,\omega/q\big)$ is shown in Figure 1.

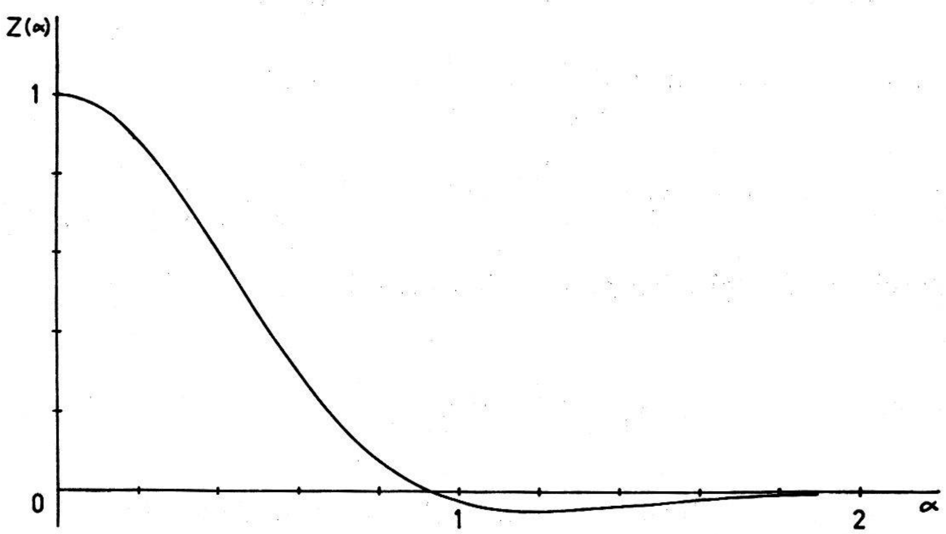


Figure 1

$Z(\alpha) = \exp(-\alpha^2)\,[1 - 2\,\alpha^2 \exp(-\alpha^2)\, {}_1F_1(1/2, 3/2; \alpha^2)]$, where $\alpha = (m\,\beta/2)^{1/2}\,(\omega/q)$. The function $F(\omega, q) = (2\,\alpha/\omega\,\pi^{1/2})\, Z(\alpha)$ is a factor in the first order correction of $S(q, \omega)$.

## 3. Extrapolations

The correction to the dynamical correlation function of the ideal gas, which is linear in the interaction, has been calculated. We have found that this correction affects the distinct part of the dynamical correlation function only, while the self part remains the same as that of the ideal gas.

The correction of the intermediate scattering function has the form:

$$\lambda\,\beta\,I^1(q,t) = -\,\varrho\,\beta\,\tilde{U}(q)\,\tilde{f}(q,t)\,.$$

We shall extrapolate this result writing (the symbol $\stackrel{\text{ex}}{=}$ means equality in the framework of an extrapolation):

$$\lambda\,\beta\,I^1(q,t) \stackrel{\text{ex}}{=} \tilde{g}_2(q)\,\tilde{f}(q,t)\,, \tag{3.1}$$

where

$$\tilde{g}_2(q) = \varrho \int d^3r\; e^{iqr}\,[g_2(r) - 1] \stackrel{1}{=} -\,\varrho\,\beta\,\tilde{U}(q)\,.$$

This extrapolation leads to the correct zeroth and second moment for arbitrary potentials [see (I.1) and (I.2)].

Transformed into configuration space equation (3.1) becomes:

$$\lambda\,\beta\,G^1(r,t) \stackrel{\text{ex}}{=} \int d^3r'\,[g_2(r') - 1]\,f(|\,\boldsymbol{r}' - \boldsymbol{r}\,|, t)\,,$$

or with (2.13)

$$1 + \lambda\,\beta\,G^1(r,t) \stackrel{\text{ex}}{=} \int d^3r'\;g_2(r')\,f(|\,\boldsymbol{r}' - \boldsymbol{r}\,|, t)\,.$$

To reach an explicit expression for $S(q,\omega)$ we make the further assumption that the self correlation function is that of the ideal gas. We then obtain:

$$S(q,\omega) \stackrel{\text{ex}}{=} S^0(q,\omega) + \lambda\,\beta\,S^1(q,\omega) \stackrel{\text{ex}}{=} \left(\frac{m\,\beta}{2\,\pi}\right)^{1/2} \frac{1}{q}\,e^{-(m\beta/2)(\omega/q)^2}$$
$$\times \left\{1 + 2\,\tilde{g}_2(q)\left[1 - m\,\beta\left(\frac{\omega}{q}\right)^2 e^{-(m\beta/2)(\omega/q)^2}\,{}_1F_1\left(\frac{1}{2}\,,\,\frac{3}{2}\,;\,\frac{m\,\beta}{2}\left(\frac{\omega}{q}\right)^2\right)\right]\right\}.$$

The qualitative behaviour of $\tilde{g}_2(q)$ for a real gas is shown in Figure 2. In Figure 3 the function:

$$Y(\alpha) = e^{-\alpha^2}\left\{1 + h\left[1 - 2\,\alpha^2\,e^{-\alpha^2}\,{}_1F_1\left(\frac{1}{2}\,,\,\frac{3}{2}\,;\,\alpha^2\right)\right]\right\},$$

is plotted for various negative values of $h = 2\,\tilde{g}_2(q)$. The function $Y(\alpha)$ and hence $S^0 + \lambda\,\beta\,S^1$ have a peak in their $\alpha$ dependence for small values of $q$ for which $2\,\tilde{g}_2(q) < -\,0{,}3$. As $h$ and therefore $q$ decreases the peak moves to the right and becomes narrower. Since the peak is localized very nearly at the value of $\alpha$ which corresponds to the sound velocity of the ideal gas ($\alpha_{id} = 9{,}11$), we conclude that this extrapolation contains the onset of sound motion. However, this extrapolation which is based on the unperturbed self part of the correlation function does not show a quasi-elastic peak.

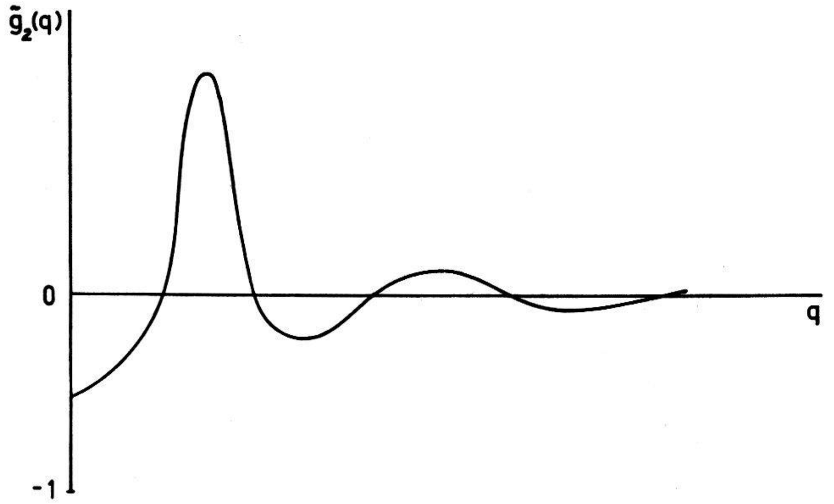


Figure 2
The distinct correlation function (schematic).

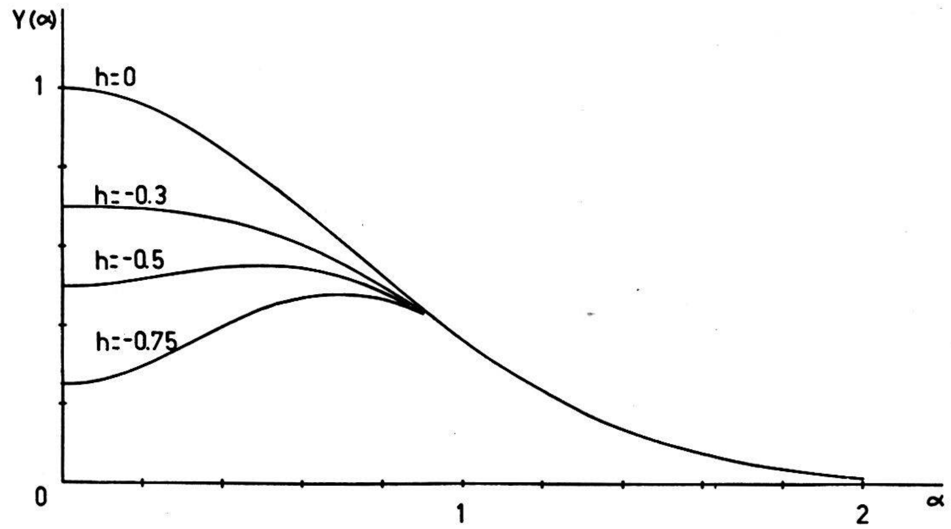


Figure 3
$S(q, \omega)$ is according to the extrapolation: $S(q, \omega) \stackrel{\text{ex}}{=} (\alpha/\omega\, \pi^{1/2})\, Y(\alpha)$.

Of course these extrapolations are speculative. The valid part of this work consists of the calculation of the first order correction of the dynamical correlation function and its Fourier transformed.

The computation of higher order corrections and partial summations may be an approach to an understanding of systems with realistic interactions. Such a calculation should, however, be preceded by a systematic study of the general term of the perturbation series. A diagrammatic representation in analogy to the perturbation theory of the quantum statistical Greens functions might be appropriate.

**Appendix I:** $\lambda\,\beta\,I^1(q,t)$

We found in Section 2 that the first order correction to the intermediate scattering function has the simple form:

$$\lambda\,\beta\,I^1(q,t) = -\,\varrho\,\beta\,\tilde{U}(q)\,\tilde{f}(q,t)\,.$$

We shall now prove that the following expansion holds:

$$\tilde{f}(q,t) = -\sum_{n=0}^{\infty} a_{2n} \left(\frac{q^2}{m\,\beta}\right)^n \frac{(i\,t)^{2n}}{(2\,n)!}\,, \tag{I.1}$$

where for $n \geqq 2$ and

a) $n$ even

$$a_{2n} = -\,[(n-1)!!]^2 + 2 \sum_{v=(2,4,\ldots,n)} (v-1)!!\,(2\,n-v-1)!!$$

with $(2\,n-1)!! = 1\cdot 3\cdot 5\cdot \ldots \cdot (2\,n-1)$ and $(-1)!! = 1$.

b) $n$ odd

$$a_{2n} = 2 \sum_{v=(2,4,\ldots,n-1)} (v-1)!!\,(2\,n-v-1)!!$$

and for $n = 0$ or $1$:

$$a_0 = -1\,,$$

$$a_2 = 0\,. \tag{I.2}$$

This will be shown by calculating the Fourier transformed of $\tilde{f}(q,t)$ with respect to time, which in section 2 was found to be $F(\omega, q)$. To this end we bring $\tilde{f}(q,t)$ into a form which permits the evaluation of the Fourier transformed.

The Gamma function $\Gamma(k)$ is defined by:

$$\Gamma(k) = \int_0^{\infty} dx\, e^{-x}\, x^{k-1}\,.$$

As $\Gamma(1/2) = \pi^{1/2}$ and $\Gamma(k+1) = k\,\Gamma(k)$ we have:

$$\Gamma\left(\frac{2\,k+1}{2}\right) = \pi^{1/2}\,\frac{(2\,k-1)!!}{2^k} \tag{I.3}$$

for $k \in Z_+^0 = \{0, 1, 2, \ldots\}$. Therefore

$$\sum_{v=(2,4,\ldots,2h)} (v-1)!!\,(2\,n-v-1)!!$$

$$= \frac{2^n}{\pi} \sum_{v=(2,4,\ldots,2h)} \int_0^{\infty} dx\, e^{-x}\, x^{(v-1)/2} \int_0^{\infty} dy\, e^{-y}\, y^{n-(v+1)/2}$$

$$= \frac{2^n}{\pi} \int_0^{\infty} dx \int_0^{\infty} dy\, e^{-(x+y)}\, x^{1/2}\, y^{n-3/2} \left[\frac{1-(x\,y^{-1})^h}{1-x\,y^{-1}}\right]. \tag{I.4}$$

From (I.2) and (I.4) $a_{2n}$ becomes for $n$ odd with $n \geqq 2$:

$$a_{2n} = \frac{2^{n+1}}{\pi} \int_0^\infty dx\, P \int_0^\infty e^{-(x+y)} \left[ \frac{x^{1/2}\, y^{n-1/2} - x^{n/2}\, y^{n/2}}{y - x} \right]$$

$$= \frac{2^{n+1}}{\pi} \int_0^\infty dx\, P \int_0^\infty dy\, e^{-(x+y)} \frac{x^{1/2}\, y^{n-1/2}}{y - x} . \quad \text{(I.5)}$$

This formula yields also for $n = 1$ the correct value:

$$a_2 = 0 .$$

Analogously for $n$ even, $n \geqq 2$ the equations (I.3) and (I.4) give

$$a_{2n} = -\frac{2^n}{\pi} \int_0^\infty dx \int_0^\infty dy\, e^{-(x+y)} (x\, y)^{(n-1)/2}$$

$$+ \frac{2^{n+1}}{\pi} \int_0^\infty dx\, P \int_0^\infty dy\, e^{-(x+y)} \left[ \frac{x^{1/2}\, y^{n-1/2} - x^{(n+1)/2}\, y^{(n-1)/2}}{x - y} \right]$$

$$= \frac{2^{n+1}}{\pi} \int_0^\infty dx\, P \int_0^\infty dy\, e^{-(x+y)} \frac{x^{1/2}\, y^{n-1/2}}{x - y} .$$

For $n = 0$ (I.5) reduces to:

$$a_0 = \frac{2}{\pi} \int_0^\infty dx\, P \int_0^\infty dy\, e^{-(x+y)} \frac{(x\, y^{-1})^{1/2}}{y - x}$$

$$= -\frac{1}{\pi} \int_0^\infty dx \int_0^\infty dy\, e^{-(x+y)} (x\, y)^{-1/2} = -1 ,$$

which is the right value for $a_0$. Thus we see that (I.5) is valid for all $n \in \mathbf{Z}_+^0$.

Combining (I.1) and (I.5) we finally obtain:

$$\tilde{f}(q, t) = -\frac{2}{\pi} \int_0^\infty dy\, P \int_0^\infty dx\, e^{-(x+y)} \frac{(x\, y^{-1})^{1/2}}{y - x} \cos \left[ q\, t \left( \frac{2}{m\, \beta} \right)^{1/2} y^{1/2} \right] . \quad \text{(I.6)}$$

Note that $\lim_{t \to \infty} f(q, t) = 0$.

We shall now compute $F(\omega, q)$ the Fourier transformed of $\tilde{f}(q, t)$:

$$F(\omega, q) = \frac{1}{2\, \pi} \int_{-\infty}^\infty dt\, e^{-i\omega t} \tilde{f}(q, t) .$$

Hence

$$F(\omega, q) = -\frac{1}{\pi} \int_0^\infty dy\, P \int_0^\infty dx\, e^{-(x+y)} \frac{(x\, y^{-1})^{1/2}}{y - x} [\delta(\omega + \alpha\, y^{1/2}) + \delta(\omega - \alpha\, y^{1/2})] ,$$

with

$$\alpha = q \left(\frac{2}{m\,\beta}\right)^{1/2} ,$$

or after substituting $z = \alpha\, y^{1/2}$ and integrating over $z$:

$$F(\omega, q) = -\frac{2}{\pi\,\alpha} e^{-(\omega/\alpha)^2} P \int_0^\infty dx\, e^{-x} \frac{x^{1/2}}{\left(\frac{\omega}{\alpha}\right)^2 - x} .$$

We now consider the integral:

$$P \int_0^\infty dx\, e^{-x} \frac{x^{1/2}}{x - s} = \operatorname*{Lim}_{\varepsilon \to 0} 2 \left[ \int_0^{(s-\varepsilon)^{1/2}} dx\, e^{-x^2} \frac{x^2}{x^2 - s} + \int_{(s+\varepsilon)^{1/2}}^\infty dx\, e^{-x^2} \frac{x^2}{x^2 - s} \right]$$

$$= 2 \int_0^\infty dx\, e^{-x^2} + 2\, s\, e^{-s} \operatorname*{Lim}_{\varepsilon \to 0} \left[ \int_0^{(s-\varepsilon)^{1/2}} dx\, e^{s-x^2} \frac{1}{x^2 - s} + \int_{(s+\varepsilon)^{1/2}}^\infty dx\, e^{s-x^2} \frac{1}{x^2 - s} \right]$$

$$= \pi^{1/2} - 2\, s\, e^{-s} \int_0^1 dy \int_0^\infty dx\, e^{y(s-x^2)} + 2\, s\, e^{-s} \operatorname*{Lim}_{\varepsilon \to 0} \left[ \int_0^{(s-\varepsilon)^{1/2}} dx \frac{1}{x^2 - s} + \int_{(s+\varepsilon)^{1/2}}^\infty dx \frac{1}{x^2 - s} \right]$$

$$= \pi^{1/2} \left(1 - s\, e^{-s} \int_0^1 dy\, e^{sy} \frac{1}{y^{1/2}}\right)$$

$$= \pi^{1/2} \left[1 - 2\, s\, e^{-s}\, {}_1F_1\left(\frac{1}{2}, \frac{3}{2}; s\right)\right] ,$$

where we have used:

$$\operatorname*{Lim}_{\varepsilon \to 0} \left[ \int_0^{(s-\varepsilon)^{1/2}} dx \frac{1}{x^2 - s} + \int_{(s+\varepsilon)^{1/2}}^\infty dx \frac{1}{x^2 - s} \right] = 0 .$$

With these results $F(\omega, q)$ is found to be:

$$F(\omega, q) = \left(\frac{2\, m\, \beta}{\pi}\right)^{1/2} \frac{1}{q} e^{-(m\beta/2)(\omega/q)^2} \times \left[1 - m\, \beta \left(\frac{\omega}{q}\right)^2 e^{-(m\beta/2)(\omega/q)^2}\, {}_1F_1\left(\frac{1}{2}, \frac{3}{2}; \frac{m\,\beta}{2} \left(\frac{\omega}{q}\right)^2\right)\right] .$$

Since the function $F(\omega, q)$ is obtained from the expression (2.11) of $F(r, t)$ by the substitution $r \to \omega$, $t \to q$ this completes the proof.

## Appendix II: The 8th moment

The exact expression for the 8th moment is an example which may be used to test considerations on the moments. Since the derivation of this expression is straightforward but rather tedious, we only state the result.

$$
\begin{aligned}
\Omega_8(q) = {} & 105 \left(\frac{q^2}{m\,\beta}\right)^4 + \frac{\varrho}{m^4} \int d^3r\, g_2(r) \\
& \times \Bigg\{ 210 \frac{q^6}{\beta^3} \frac{\partial^2 U(r)}{\partial x^2} + (39 \cos q\,x + 27) \frac{q^4}{\beta^3} \frac{\partial^4 U(r)}{\partial x^4} \\
& + (91 + 35 \cos q\,x) \frac{q^4}{\beta^2} \left[\frac{\partial^2 U(r)}{\partial x^2}\right]^2 + 72 (\sin q\,x) \frac{q^3}{\beta^2} \frac{\partial^2 U(r)}{\partial x^2} \frac{\partial^3 (U r)}{\partial x^3} \\
& + 4\,(1 - \cos q\,x) \frac{q^2}{\beta} \left[\frac{\partial^2 U(r)}{\partial x^2}\right]^3 + 12\,(1 - \cos q\,x) \frac{q^2}{\beta^2} \left[\frac{\partial^3 U(r)}{\partial x^3}\right]^2 \Bigg\} \\
& + \frac{\varrho^2}{m^4} \int d^3r\, d^3r'\, g_3(\mathbf{r}, \mathbf{r}') \\
& \times \Bigg\{ 63 \frac{q^4}{\beta^2} \frac{\partial^2 U(r)}{\partial x^2} \frac{\partial^2 U(r')}{\partial x'^2} + 6\,[7 \sin q\,x - \sin q(x - x')] \frac{q^3}{\beta^2} \frac{\partial^3 U(r)}{\partial x^3} \frac{\partial^2 U(r')}{\partial x'^2} \\
& + 3\,[\cos q(x - x') - 2 \cos q\,x + 1] \frac{q^2}{\beta^2} \frac{\partial^3 U(r)}{\partial x^3} \frac{\partial^3 U(r')}{\partial x'^3} \\
& + 2\,[3 + 2 \cos q(x - x') - 2 \cos q\,x' - 3 \cos q\,x] \frac{q^2}{\beta} \left[\frac{\partial^2 U(r)}{\partial x^2}\right]^2 \frac{\partial^2 U(r')}{\partial x'^2} \\
& + (\cos q\,x - 1) \frac{q^2}{\beta} \frac{\partial^2 U(r)}{\partial x^2} \frac{\partial^2 U(r')}{\partial x'^2} \frac{\partial^2 U(|\mathbf{r} - \mathbf{r}'|)}{\partial (x - x')^2} \Bigg\} \\
& + \frac{\varrho^3}{m^4} \int d^3r\, d^3r'\, d^3r''\, g_4(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \\
& \times \Bigg\{ [1 + \cos q(x - x') - 2 \cos q\,x] \frac{q^2}{\beta} \frac{\partial^2 U(r)}{\partial x^2} \frac{\partial^2 U(r')}{\partial x'^2} \frac{\partial^2 U(r'')}{\partial x''^2} \\
& + [2 \cos q\,x' - \cos q\,x - \cos q(x' - x'')] \frac{q^2}{\beta} \frac{\partial^2 U(r)}{\partial x^2} \frac{\partial^2 U(r')}{\partial x'^2} \frac{\partial^2 U(|\mathbf{r}'' - \mathbf{r}|)}{\partial (x'' - x)^2} \Bigg\} .
\end{aligned}
$$

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