SHORT TIME BEHAVIOUR OF DENSITY CORRELATION FUNCTIONS

H. H. U. KONIJNENDIJK

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Henricus Hubertus Ursinus Konijnendijk
natuurkundig ingenieur
geboren te 's-Gravenhage

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Dit proefschrift is goedgekeurd door de promotor:

Prof.dr. J.M.J. van Leeuwen

Aan Ankie

Aan mijn ouders

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INTRODUCTION

Time dependent correlation functions play an important role in the theories that describe the dynamical behaviour of fluids and gases. It is well known that macroscopic transport coefficients, such as the diffusion coefficient, can be expressed as time integrals over these correlation functions (Forster, Martin, 1970). The most important correlation functions are the density-density correlation function $G(\vec{r},t)$, introduced by van Hove (1954), and the velocity autocorrelation function $C_D(t)$. Classically $G(\vec{r},t)$ is proportional to the probability that there is a particle at time t and position $\vec{r}$ given that there was some particle at $t = 0$ in the origin. Experimentally the fourier transform of $G(\vec{r},t)$ with respect to the position $\vec{r}$ and the time t, the so-called scattering function $S(k,\omega)$, can be obtained by slow neutron scattering on noble gases (Andriesse, 1970; Hasman, 1973; Lefevre, Chen, Yip, 1972). Time dependent correlation functions can also be calculated by means of molecular dynamics (Verlet, 1967).

Theoretically the exact calculation of the time dependent correlation functions is only possible for the two following totally different time domains:

a) For short times it is possible to make a time expansion of the correlation functions, the so-called moments expansion (de Gennes, 1959). Only the first few moments are exactly known in terms of the static correlation functions. The time domain in which this expansion is useful is restricted by the shortest microscopic time scale present. In fluids, where the molecules undergo sudden collisions, this is the duration of the collision, which may be extremely small (10^{-14} s), much smaller for instance than the mean free time in moderately dense gases.

b) For large times the hydrodynamic equations become valid. Then a complete description of the correlation functions is possible in terms of the transport coefficients of the fluid. The hydrodynamic time domain is restricted from below by the largest microscopic time scale. For a moderately dense gas this is the mean free time.

Thus a gap exists in the time domain where no rigorous description is possible. For dense fluids the gap is small enough that one may try an interpolation scheme as for instance suggested by Jhon e.a. (1975). For more dilute gases the gap is much too wide and a kinetic approach seems more appropriate.

Neutron scattering experiments for low density systems are possible on well chosen systems such as Ar^{36} (Andriesse, 1970) which has a very large scattering cross section. The time scale of such an experiment is precisely of the order of the mean free time, so that the most important contribution to the correlation function for these times comes from the collisions in which only two particles are involved.

The conventional Boltzmann equation cannot be used for an adequate description of the detailed time dependence of the correlation functions, because in the Boltzmann collision operator the collisions are treated in an asymptotic way (as cross sections), where as the correlation functions have a time scale in which the duration of the collision may not be taken zero.

The Boltzmann equation may be modified (Mazenko, 1973, 1974) such as to treat the individual collisions in full detail and the solution of this modified equation provides the full time dependence of the correlation functions in the low density limit.

The solution of the modified Boltzmann equation is however quite involved and in this thesis we present a simpler approach with a more limited scope: to extend the calculation of the correlation functions for moderately dense gases up to a time scale of the order of a mean free time. For this purpose we have used the Ursell-expansion of the correlation functions; in this expansion the successive terms describe the effect of an increasing number of colliding particles. The first term contains only the free streaming of the particles yielding the ideal gas behaviour of the correlation functions. The second term represents the effect of the two particle collisions, so this term gives the most dominant contribution to the deviation of the correlation function from its ideal gas value for times up to the mean free time.

As a first approximation for a real gas we have taken a hard spheres system, which has the advantage that the mathematical expressions, that describe the two particle collision, are very easy. A disadvantage is however that the duration of the collision is zero, so that the moments expansion is not valid; it has to be replaced by a modified moments expansion, which can be obtained from an extension of the hard spheres Liouville operator (Ernst et. al., 1969). Because the replacement of the true potential by the hard spheres interaction is rather drastic, we expect that our theoretically calculated correlation functions agree with the experimentally measured functions only in a qualitative way. Therefore we have also done calculations for a system of particles with a Lennard-Jones interaction, which accounts very well for the equilibrium properties of noble gases like argon (Verlet, 1976, 1968). These calculations are however more complicated because the equations of motion can only numerically be solved on a computer.

This dissertation is divided into four chapters. Chapter 1 contains the definitions of the correlation functions and a short discussion of the moments expansion. In chapter 2 the Ursell expansion is derived. In chapter 3 the Ursell expansion of the hard spheres system is discussed, while in chapter 4 our theoretically calculated correlation functions for a Lennard-Jones interaction are compared with correlation functions, obtained by neutron scattering and by molecular dynamics.

CHAPTER 1

DEFINITION AND PROPERTIES OF THE SYSTEM

1.1 DEFINITIONS

We consider a classical one-component monatomic system consisting of N particles of mass m enclosed in a volume V. Assuming that one has only two-particle interactions the Hamilton function $H(\Gamma)$ of this system is:

$$H(\Gamma) = \sum_{i=1}^{N} p_i^2/2m + \frac{1}{2} \sum_{i \neq j}^{N} \sum \varphi(r_{ij}) \qquad (1.1)$$

where $\vec{p}_i$ and $\vec{r}_i$ are the momentum and the position of the i'th particle, Γ stands for the collection of momenta and coordinates $\vec{p}_1,\vec{r}_1,\vec{p}_2,\vec{r}_2,\ldots,\vec{p}_N,\vec{r}_N$ and $\varphi(r_{ij})$ is the interaction between the particles i and j on a distance $r_{ij} = |\vec{r}_i-\vec{r}_j|$.

Given the Hamilton function $H(\Gamma)$ one can calculate the canonical ensemble average of an arbitrary function $f(\Gamma)$ in the phase space as:

$$\langle f(\Gamma)\rangle = \int d\Gamma \; \rho(\Gamma) f(\Gamma) \qquad (1.2)$$

where the phase space density $\rho(\Gamma)$ is given by:

$$\rho(\Gamma) = \exp(-\beta H(\Gamma)) \; / \int d\Gamma \; \exp(-\beta H(\Gamma)) \qquad (1.3)$$

with $\beta = 1/k_BT$, k_B is Boltzmann's constant and T is the absolute temperature.

In the following chapters we shall frequently make use of some equilibrium distribution functions such as the Maxwell-Boltzmann momentum distribution function $\phi(p)$:

$$\phi(p) = (\beta/2\pi m)^{\frac{3}{2}} \; e^{-\beta p^2/2m} \qquad (1.4)$$

and the m-particle static correlation function $g(\vec{r}_1\vec{r}_2\ldots\vec{r}_m)$, defined as (Münster, 1969):

$$n^m g(\vec{r}_1\vec{r}_2..\vec{r}_m)=N(N-1)..(N-m+1)Q_N^{-1}\int d\vec{r}_{m+1}...d\vec{r}_N \exp(-\beta\Phi(\vec{r}^N)) \quad (1.5)$$

where n = N/V is the number density, $\Phi(\vec{r}^N) = \Phi(\vec{r}_1...\vec{r}_N)$ is the potential energy:

$$\Phi(\vec{r}^N) = \frac{1}{2}\sum_{i\neq j}\sum \varphi(r_{ij}), \quad (1.6)$$

and Q_N is the configuration integral, given by:

$$Q_N = \int d\vec{r}_1...d\vec{r}_N \exp(-\beta\Phi(\vec{r}^N)) \quad (1.7)$$

Of particular interest for the two-particle problem is the two-particle distribution function $g(\vec{r}_1\vec{r}_2)$, also called the pair or radial distribution function which depends only on the relative distance r_{12} of both particles in an isotropic system. The pair correlation function g(r) gives the difference of the probability to find a particle at a distance r from the origin, given that there is at the same time another particle in the origin, and the probability to find both particles at distance r in a completely random distribution.

The difference between the pair correlation function g(r) and its asymptotic value one will be called G(r):

$$G(r) = g(r)-1, \quad (1.8)$$

which has the following fourier transform (with respect to the spatial variable $\vec{r}$):

$$n\int d\vec{r}\, e^{-i\vec{k}.\vec{r}}\, G(r) = n\,\tilde{G}(k) = S(k)-1 \quad (1.9)$$

where S(k) is the structure factor which can be directly measured by slow neutron scattering.

Another important two-particle distribution function is the direct correlation function C(r) that is defined implicitly in terms of G(r) in the Ornstein-Zernike equation (Rice and Gray, 1965):

$$G(r) = C(r) + n \int d\vec{r}\,' \, C(|\vec{r}-\vec{r}\,'|)G(r') \tag{1.10}$$

From (1.9) and the fourier transform of (1.10) it follows that the structure factor S(k) can also be obtained from:

$$S(k) = (1-n\,\tilde{C}(k))^{-1} \tag{1.11}$$

with $\tilde{C}(k)$ the fourier transform of C(r).

Because the following chapters concern with time dependent correlation functions the time evolution of the system is of great importance. The trajectory $\Gamma(t)$ of the N-particle system in phase space is generated by the streaming operator $S_t(1..N)$. If one has at t = 0 some arbitrary function $f(\Gamma)$ of the phase space coordinates $\Gamma = (\vec{p}_1..\vec{p}_N,\vec{r}_1..\vec{r}_N)$, this function will have at time t the value:

$$f(\Gamma(t)) = S_t(1..N)f(\Gamma) \tag{1.12}$$

In the case of a non-singular interaction potential S_t is given by (Balescu, 1975):

$$S_t = \exp(tL_N) \tag{1.13}$$

where the Liouville operator L_N is the Poisson bracket with the Hamilton function:

$$\begin{aligned} L_N = L(1..N) &= \sum_{i=1}^{N} \left(\frac{\partial H}{\partial \vec{p}_i} \cdot \frac{\partial}{\partial \vec{r}_i} - \frac{\partial H}{\partial \vec{r}_i} \cdot \frac{\partial}{\partial \vec{p}_i}\right) \\ &= L_o(1..N) + \frac{1}{2}\sum_{i\neq j}\sum L_I(ij) \end{aligned} \tag{1.14}$$

One observes that L_N consists of the free streaming part

$$L_o(1..N) = \sum_{i=1}^{N} L_o(i) = \sum_{i=1}^{N} \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{r}_i} \qquad (1.15)$$

and an interaction part containing terms like:

$$L_I(ij) = \left(\frac{\partial}{\partial \vec{p}_j} - \frac{\partial}{\partial \vec{p}_i}\right) \cdot \frac{\partial \varphi(r_{ij})}{\partial \vec{r}_i} \qquad (1.16)$$

The hermitian conjugate $L^{\dagger}$ of the Liouville operator L with respect to the weight function $\rho(\Gamma)$, given in (1.3), will be defined by:

$$\int d\Gamma\ \rho(\Gamma) f(\Gamma) L\ g(\Gamma) = \int d\Gamma\ \rho(\Gamma) g(\Gamma) L^{\dagger} f(\Gamma) \qquad (1.17)$$

where $f(\Gamma)$ and $g(\Gamma)$ are arbitrary functions of phase space. By partial integration one can easily verify that L is antihermitian:

$$L^{\dagger} = -L \qquad (1.18)$$

In the case of the singular hard spheres interaction, defined by:

$$\begin{aligned} \varphi(r) &= \infty \qquad r < \sigma \\ &= 0 \qquad r \geq \sigma \end{aligned} \qquad (1.19)$$

with σ the diameter of the spheres, one sees from (1.16) that the definition (1.13) for the streaming operator makes little sense. Another expression for S_t is given by Ernst et al. (1969) in terms of "pseudo" Liouville operators $L_{\pm}$. For forward resp. backward streaming they obtained the following streaming operators:

$$\begin{aligned} S_t &= \exp(tL_+) \qquad t \geq 0 \\ &= \exp(tL_-) \qquad t < 0 \end{aligned} \qquad (1.20)$$

with $L_\pm$ given as:

$$L_\pm = L_o \pm \frac{1}{2} \sum_{i \neq j}\sum T_\pm(ij) = L_o \pm L'_\pm \qquad (1.21)$$

Here L_o is the free streaming part (1.15) of the Liouville operator and the $T_\pm$ operators are defined as:

$$T_\pm(ij) = |\vec{v}_{ij} \cdot \hat{r}_{ij}|\theta(\mp\vec{v}_{ij} \cdot \vec{r}_{ij})\delta(r_{ij}\ \sigma)(b_{ij}-1) \quad (1.22)$$

where $\vec{v}_{ij} = \vec{p}_{ij}/m = (\vec{p}_i-\vec{p}_j)/m$, $\hat{r}_{ij} = \vec{r}_{ij}/r_{ij}$, $\theta(x)$ is the unit step function:

$$\theta(x) = 0 \qquad x < 0$$
$$\quad = 1 \qquad x \geq 0 \qquad (1.23)$$

and the operator b_{ij} changes the initial momenta $\vec{p}_i,\vec{p}_j$ into those after the collision $\vec{p}'_i,\vec{p}'_j$ according to:

$$b_{ij}f(\vec{p}_1,\vec{r}_1,\ldots,\vec{p}_i,\vec{r}_i,\ldots,\vec{p}_j,\vec{r}_j,\ldots,\vec{p}_N,\vec{r}_N) =$$
$$= f(\vec{p}_1,\vec{r}_1,\ldots,\vec{p}'_i,\vec{r}_i,\ldots,\vec{p}'_j,\vec{r}_j,\ldots,\vec{p}_N,\vec{r}_N) \qquad (1.24)$$

with

$$\vec{p}'_i = \vec{p}_i - (\vec{p}_{ij} \cdot \hat{r}_{ij})\hat{r}_{ij}$$
$$\vec{p}'_j = \vec{p}_j + (\vec{p}_{ij} \cdot \hat{r}_{ij})\hat{r}_{ij} \qquad (1.25)$$

As the fact that different Liouville operators are needed for forward ($t>0$) and backward ($t<0$) streaming may seem a little bit strange we shall give here a short comment. One sees immediately that the collisional part of a hard sphere Liouville operator should be defined at the point of contact $r_{ij} = \sigma$. In Γ-space two sets of these points can be distinguished, namely those where the relative velocity $\vec{v}_{ij}$ has the same direction as the relative contact vector $\vec{r}_{ij}$ ($\vec{v}_{ij} \cdot \vec{r}_{ij}>0$) and those where $\vec{v}_{ij} \cdot \vec{r}_{ij}<0$. The first case refers to backward streaming (because the particles have already collided), the latter one to forward streaming (because the particles are going to collide). So it is clear that the relevant Γ-spaces for forward and backward streaming are not the same. One should declare an operator zero in the region where it does not apply as is done in (1.22) by means of the step functions $\theta(\mp\vec{v}_{ij} \cdot \vec{r}_{ij})$. Thus it is impossible to make use of the same analytical expression in the whole Γ-space.

This has also a consequence for the hermitian conjugate $L_+^\dagger$ of the pseudo Liouville operator with respect to the canonical ensemble average. For the hard spheres interaction the following relation can be derived:

$$L_+^\dagger = -L_- \qquad (1.26)$$

The detailed calculation of this hermitian conjugate will be given in appendix A.

A summary of all relations that are important with respect to the hard spheres streaming operator can be found in table I.

1.2 TIME DEPENDENT CORRELATION FUNCTIONS

The time dependent density-density correlation function $G(\vec{r}-\vec{r}\,';t)$ and the self part $G^s(\vec{r}-\vec{r}\,';t)$, which are of interest for neutron scattering, are defined by (van Hove, 1954):

$$G(\vec{r}-\vec{r}\,';t) = n^{-1}\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\vec{r}_i-\vec{r})\,\delta(\vec{r}_j(t)-\vec{r}\,')\rangle$$

and (1.27)

$$G^s(\vec{r}-\vec{r}\,';t) = n^{-1}\langle \sum_{i=1} \delta(\vec{r}_i-\vec{r})\,\delta(\vec{r}_i(t)-\vec{r}\,')\rangle$$

with $\vec{r}_i$ the position of particle i at t = 0 and $\vec{r}_j(t)$ the posi-

Table I. The hard spheres streaming operator.

Forward streaming (t>0)	$S_t = \exp(tL_+)$
Backward streaming (t<0)	$S_t = \exp(tL_-)$
Pseudo Liouville operator	$L_\pm = L_o \pm L'_\pm$
Free streaming part	$L_o = \sum_{i=1}^{N} \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{r}_i}$
Interaction part	$L'_\pm = \frac{1}{2} \sum_{i \neq j}\sum T_\pm(ij)$

$$T_\pm(ij) = |\vec{v}_{ij} \cdot \hat{r}_{ij}|\,\theta(\mp\vec{v}_{ij} \cdot \vec{r}_{ij})\,\delta(r_{ij}-\sigma)\,(b_{ij}-1)$$

with

$$\vec{v}_{ij} = \vec{p}_{ij}/m = (\vec{p}_i-\vec{p}_j)/m \quad \text{and} \quad \hat{r}_{ij} = \vec{r}_{ij}/r_{ij}$$

Collision operator b_{ij}:

$$b_{ij}f(\vec{p}_1,\vec{r}_1,\ldots,\vec{p}_i,\vec{r}_i,\ldots,\vec{p}_j,\vec{r}_j,\ldots,\vec{p}_N,\vec{r}_N)$$

$$= f(\vec{p}_1,\vec{r}_1,\ldots,\vec{p}\,'_i,\vec{r}_i,\ldots,\vec{p}\,'_j,\vec{r}_j,\ldots,\vec{p}_N,\vec{r}_N)$$

with

$$\vec{p}\,'_i = \vec{p}_i-(\vec{p}_{ij} \cdot \hat{r}_{ij})\hat{r}_{ij}$$

$$\vec{p}\,'_j = \vec{p}_j+(\vec{p}_{ij} \cdot \hat{r}_{ij})\hat{r}_{ij}$$

Hermitian conjugate defined by: $\langle fL_+g\rangle = \langle (L_+^\dagger f)g\rangle$

$$L_+^\dagger = -L_-$$

tion of particle j at time t. $G(\vec{r}-\vec{r}';t)$ is proportional to the probability to find a particle at position $\vec{r}'$ and time t given that there was at t = 0 a particle at $\vec{r}$. The self function $G^s(\vec{r}-\vec{r}';t)$ refers to the case that both particles are identical.

For convenience we will consider the fourier transforms (with respect to the spatial variable $\vec{r}$) of these correlation functions, which are called the intermediate scattering functions:

$$F_k(t) = \int d\vec{r}\ \exp(-i\vec{k}.\vec{r})G(\vec{r};t)$$

$$= N^{-1}\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(-i\vec{k}.\vec{r}_i)\exp(i\vec{k}.\vec{r}_j(t))\rangle$$

and (1.28)

$$F_k^s(t) = N^{-1}\langle \sum_{i=1}^{N} \exp(-i\vec{k}.\vec{r}_i)\exp(i\vec{k}.\vec{r}_i(t))\rangle$$

With (1.5) and (1.9) it is easy to verify that their initial values are:

$$F_k(0) = S(k)$$

(1.29)

$$F_k^s(0) = 1$$

The intermediate scattering function $F_k(t)$ and its self part $F_k^s(t)$ are often referred to as the coherent and incoherent intermediate scattering function. Their fourier transforms with respect to the time are called the coherent and incoherent scattering functions, $S(k,\omega)$ resp. $S^s(k,\omega)$. They can be measured by slow neutron scattering. The expressions (1.28) for $F_k(t)$ and $F_k^s(t)$ will frequently be used in another form by introducing the streaming operator $S_t = \exp(tL)$ ((1.12) and (1.13)). They take then the following form:

$$F_k(t) = N^{-1}\langle \sum_{i=1}^{N} \exp(-i\vec{k}.\vec{r}_i)\exp(tL) \sum_{j=1}^{N} \exp(i\vec{k}.\vec{r}_j)\rangle$$

and (1.30)

$$F_k^s(t) = N^{-1} \langle \sum_{i=1}^{N} \exp(-i\vec{k}.\vec{r}_i)\exp(tL)\exp(i\vec{k}.\vec{r}_i) \rangle$$

The calculation of $F_k(t)$ and $F_k^s(t)$ for free particles is very easy and yields:

$$F_k(t) = F_k^s(t) = \exp(-k^2t^2/2\beta m) \qquad (1.31)$$

Because we are interested in the differences between the correlation functions of a gas of interacting particles and those of an ideal gas, we shall, instead of $F_k(t)$ and $F_k^s(t)$ itself, calculate their deviations $\varepsilon_k(t)$ and $\varepsilon_k^s(t)$ from the ideal gas values. So we write:

$$F_k(t) = S(k)[\exp(-k^2t^2/2\beta m)+\varepsilon_k(t)]$$

and (1.32)

$$F_k^s(t) = \exp(-k^2t^2/2\beta m)+\varepsilon_k^s(t)$$

Comparing this with (1.29) one sees immediately that the initial values of the deviations are:

$$\varepsilon_k(0) = \varepsilon_k^s(0) = 0 \qquad (1.33)$$

Another correlation function that we will consider is the velocity autocorrelation function $C_D(t)$:

$$C_D(t) = \langle\vec{v}(0) \cdot \vec{v}(t)\rangle/\langle\vec{v}(0) \cdot \vec{v}(0)\rangle \qquad (1.34)$$

where $\vec{v}$ is the velocity of some particle, say particle 1. For free streaming particles $C_D(t) = 1$. Finally we shall give a relation between $C_D(t)$ and the second derivative of $F_k^s(t)$ (Egelstaff, 1967):

$$C_D(t) = -\beta m \lim_{k\to 0} \frac{1}{k^2} \frac{\partial^2 F_k^s(t)}{\partial t^2} \qquad (1.35)$$

This relation enables us to calculate the velocity autocorrelation function $C_D(t)$ if the incoherent intermediate scattering function is known.

1.3 THE MOMENTS OF THE CORRELATION FUNCTIONS

One possibility to obtain a short time expansion of correlation functions is to expand these functions in a power series in the time t. For the intermediate scattering functions this can be accomplished by substituting in (1.30) for the streaming operator the series expansion of the exponent:

$$\exp(tL) = \sum_{n=0}^{\infty} t^n L^n / n! \qquad (1.36)$$

So we may write:

$$F_k(t) = \sum_{n=0}^{\infty} M_n(k) t^n / n!$$
$$F_k^s(t) = \sum_{n=0}^{\infty} M_n^s(k) t^n / n! \qquad (1.37)$$

and in the same way for the velocity autocorrelation function:

$$C_D(t) = \sum_{n=0}^{\infty} C_n t^n / n! \qquad (1.38)$$

The expansion coefficients are often referred to as the moments or the sum rules. Calculations of de Gennes (1959) show for the first few moments of the intermediate scattering function:

$$M_o(k) = S(k)$$
$$M_2(k) = -k^2/\beta m \qquad (1.39)$$
$$M_4(k) = k^4 (m^2\beta)^{-1} [\, 3/\beta + nk^{-4} \int d\vec{r} g(r)(1-\cos\vec{k}.\vec{r})(\vec{k}.\vec{\nabla})^2 \varphi(r)]$$

For the incoherent intermediate scattering function they become:

$$M_o^s(k) = 1$$

$$M_2^s(k) = -k^2/\beta m \tag{1.40}$$

$$M_4^s(k) = k^4(m^2\beta)^{-1}[(3/\beta)+(n/3k^2)\int d\vec{r}\ g(r)\vec{\nabla}^2\varphi(r)]$$

and for the velocity autocorrelation function:

$$C_o = 1$$

$$C_2 = -(n/3m)\int d\vec{r}\ g(r)\vec{\nabla}^2\varphi(r) \tag{1.41}$$

The higher order moments contain three and more particle correlation functions that are only roughly known.

These expressions hold only for non-singular interactions. In that case also all odd moments vanish and the moments of $F_k(t)$ and $F_k^s(t)$ can be expressed in terms of their time fourier transforms, the scattering functions $S(k,\omega)$ and $S^s(k,\omega)$. From (1.37) one sees immediately that:

$$M_n(k) = \left(\frac{\partial^n F_k(t)}{\partial t^n}\right)_{t=0}$$

$$= \left(\frac{\partial^n}{\partial t^n}\int_{-\infty}^{\infty} d\omega\ e^{-i\omega t}\ S(k,\omega)\right)_{t=0}$$

$$= (-i)^n\int_{-\infty}^{\infty} d\omega\ \omega^n S(k,\omega) \tag{1.42}$$

and for the incoherent function:

$$M_n^s(k) = (-i)^n\int_{-\infty}^{\infty} d\omega\ \omega^n S^s(k,\omega)$$

The usefulness of these series is determined by their convergence. An indication of the convergence can be obtained by studying the relative magnitude of the successive terms. To see under which conditions this series expansion is worthwhile we shall calculate the ratio of the fourth and the second moment of the self function. From (1.40) it is found that:

$$M_4^s/M_2^s = -3k^2/\beta m - n/(3m) \int d\vec{r}\; g(r)\vec{\nabla}^2\varphi(r) \qquad (1.43)$$

For small densities g(r) can be approximated by:

$$g(r) \simeq \exp(-\beta\varphi(r))$$

and we find for the integral in the right hand side of (1.43):

$$\int d\vec{r}\; \exp(-\beta\varphi(r))\vec{\nabla}^2\varphi(r)$$

Integrating this once partially, we get:

$$- \int d\vec{r}\{\vec{\nabla}\exp(-\beta\varphi(r))\} \cdot \vec{\nabla}\varphi(r)$$

$$= \beta \int d\vec{r}\; \exp(-\beta\varphi(r))\; [\vec{\nabla}\varphi(r)]^2$$

$$\simeq \beta \int d\vec{r}\; g(r)\; [\vec{\nabla}\varphi(r)]^2$$

and this is essentially the average of the square of the intermolecular force. One sees that the range of validity of the time expansion is smaller when k becomes larger and when we have to do with stronger forces.

In the case of the hard spheres interaction (and also for other singular potentials) the force is infinite on the sphere and from (1.39), (1.40) and (1.41) it follows that $M_4(k)$, $M_4^s(k)$ and C_2 are infinite. This means that the moments expansion diverges for this singular interaction. An alternative for hard spheres can be found by using, instead of the singular Liouville operator L, the pseudo Liouville operators $L_\pm$ defined in (1.21).

From (1.12), (1.20) and (1.28) it is seen that the intermediate scattering function takes the following form for $t \geq 0$:

$$F_k(t) = N^{-1}\langle \sum_{i=1}^{N} \exp(-i\vec{k}.\vec{r}_i)\exp(tL_+) \sum_{j=1}^{N} \exp(i\vec{k}.\vec{r}_j)\rangle \quad (1.44)$$

The moments are obtained by making a Taylor expansion of the exponentional streaming operator. Because the calculations are rather complicated they will be carried out in appendix B. The results are for $F_k(t)$:

$$M_o(k) = S(k)$$

$$M_1(k) = 0$$

$$M_2(k) = -k^2/\beta m \quad (1.45)$$

$$M_3(k) = 8\pi^{\frac{1}{2}} n\, g(\sigma)/(3(\beta m)^{\frac{3}{2}})\, [\, (k\sigma)^2 -$$

$$- 3k\sigma \sin k\sigma - 6\cos k\sigma + 6(\sin k\sigma)/k\sigma]$$

We see that the hard spheres moments up to the second moment are exactly the same as the moments (1.39) of a system with a continuous potential. The reason is that every system behaves like an ideal gas for very short times because the particles do not feel the interaction yet. But the intermediate scattering function is for these very short times just determined by the first few moments, so the first hard spheres moments have to correspond with those of the ideal gas, just as the first moments of a system with a continuous potential. The appearance of uneven moments, like the third moment, is due to the fact that during a hard spheres collision the velocity changes instantaneously and the force between the particles is infinite (Sears, 1972).

The calculations of the first moments of the self part of the hard spheres intermediate scattering function are also carried out in appendix B and yield:

$$M_o^s(k) = 1$$

$$M_1^s(k) = 0$$

$$M_2^s(k) = -k^2/\beta m \qquad (1.46)$$

$$M_3^s(k) = 8\pi^{\frac{1}{2}} n\, g(\sigma)(k\sigma)^2/(3(\beta m)^{\frac{3}{2}})$$

The first moments of the velocity autocorrelation function. become:

$$C_o = 1$$

$$C_1 = -8\pi^{\frac{1}{2}} n\sigma^2\, g(\sigma)/(3(\beta m)^{\frac{1}{2}}) \qquad (1.47)$$

The fourth and higher order moments contain integrals over 3- and more particle distribution functions, so they cannot be calculated exactly yet. Recently de Schepper and Cohen (1976) have succeeded to give an expression for C_2, valid for low densities.

CHAPTER 2

THE URSELL EXPANSION OF THE CORRELATION FUNCTIONS

In this section we will give a systematic expansion of the above defined correlation functions where the successive terms involve an increasing number of colliding particles. The first term gives the ideal gas, the second term the effect of the two particle collisions in time t and so on.

To do this we first introduce the expansion of the streaming operator S_t that describes the trajectory $\Gamma(t)$ of the system in phase space. The next section will be concerned with the straightforward expansion of the correlation functions. Because we are interested in the short time behaviour, where the most important contributions come from the two particle collisions, we will derive some detailed expressions of the two particle terms in these expansions. However, it will appear that the expression for the intermediate scattering function consists of two parts, one of which contains the static triple distribution function. Because there is little known of this distribution function it is necessary to make an approximation for it. It will be shown that as a consequence of this approximation the second and higher moments do not agree with the exact moments.

To avoid this disagreement in the last sections another expansion of the correlation functions will be derived taking as a starting point the second derivative of the intermediate scattering functions and making use of the antihermiticity of the Liouville operator. In this approach no approximations for the static correlation functions are needed and it will be proved that the zeroth, second and fourth moments of the two particle terms correspond with the exact moments.

2.1 THE URSELL EXPANSION OF THE STREAMING OPERATOR

In order to obtain the desired expansion of the correlation functions we make use of the Ursell expansion (Cohen, 1968;

van Leeuwen and Yip, 1965) of the streaming operator S_t:

$$S_t(1...N) = U_t(1)U_t(2) \; ... \; U_t(N) \qquad (2.1)$$

$$+ \sum_{\{j_1j_2\}} U_t(j_1j_2)U_t(1)...U_t(j_1-1)U_t(j_1+1)...$$

$$...U_t(j_2-1)U_t(j_2+1)...U_t(N)$$

$$+ \sum_{\{j_1j_2j_3\}} U_t(j_1j_2j_3)U_t(1)...U_t(j_1-1)U_t(j_1+1)...$$

$$...U_t(j_2-1)U_t(j_2+1)...U_t(j_3-1)U_t(j_3+1)...U_t(N)+...$$

with

$$U_t(1) = S_t(1) = S_t^o(1)$$

$$U_t(12) = S_t(12 - S_t^o(12)$$

$$U_t(123) = S_t(123) - S_t(12)S_t^o(3) - S_t(13)S_t^o(2) \qquad (2.2)$$

$$- S_t(23)S_t^o(1) + 2S_t^o(123)$$

Here is $S_t^o(1..m)$ the free streaming operator of m particles, so

$$S_t^o(1..m) = \exp(tL_o(1..m)) \qquad (2.3)$$

In (2.1) $\{j_1j_2\}$ means all pairs of particles (j_1,j_2), $\{j_1j_2j_3\}$ all combinations of three different particles (j_1,j_2,j_3) etc. $U_t(1)$ describes the free streaming of particle 1. $U_t(12)$ gives the effect of the interaction between the particles 1 and 2 on their trajectories, because the free streaming of the both particles is subtracted. Analogously $U_t(123)$ gives the difference between the situation that all three particles collide and the situations that one particle is free streaming while both of the other particles may or may not be colliding.

2.2 THE URSELL EXPANSION OF THE CORRELATION FUNCTIONS

In this section we shall derive expressions for the Ursell expansion of the intermediate scattering functions $F_k(t)$ and $F_k^s(t)$ and the velocity autocorrelation function $C_D(t)$. Let us start with $F_k(t)$, given in (1.28) by:

$$F_k(t) = N^{-1} \langle \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(-i\vec{k}\cdot\vec{r}_i)\exp(i\vec{k}\cdot\vec{r}_j(t))\rangle \quad (2.4)$$

With (2.1) the expression $\exp(i\vec{k}\cdot\vec{r}_j(t))$ can be written as:

$$\exp(i\vec{k}\cdot\vec{r}_j(t)) = S_t(1..N)\exp(i\vec{k}\cdot\vec{r}_j)$$

$$= [U_t(j)+\sum_{j_1}{}' U_t(jj_1) + \frac{1}{2}\sum_{j_1 j_2}{}' U_t(jj_1j_2)+..]\exp(i\vec{k}\cdot\vec{r}_j)$$

$$= [U_t(j)+\sum_{m=1}^{N-1}\frac{1}{m!}\sum_{j_1j_2..j_m}{}' U_t(jj_1..j_m)]\exp(i\vec{k}\cdot\vec{r}_j) \quad (2.5)$$

where use has been made of:

$$U_t(j_1)\exp(i\vec{k}\cdot\vec{r}_j) = \exp(i\vec{k}\cdot\vec{r}_j) \quad \text{for} \quad j_1 \neq j$$

because the free streaming of particle j_1 does not influence the streaming of particle j. In (2.5) the primes over the summation signs indicate that the summation indices must be different to each other and may also not be equal to j; the factor m! is inserted to avoid double counting. Substituting (2.5) in (2.4) one obtains for the intermediate scattering function:

$$F_k(t) = N^{-1}\langle \sum_{i=1}^{N}\sum_{j=1}^{N}\exp(-i\vec{k}\cdot\vec{r}_i)\,[U_t(j) + \sum_{m=1}^{N-1}\frac{1}{m!}\sum_{j_1j_2..j_m}{}' U_t(jj_1..j_m)]\exp(i\vec{k}\cdot\vec{r}_j)\rangle \quad (2.6)$$

and an analogous expression for the self function. This expression is symmetric in the indices $j,j_1,..,j_m$, so one can label particle j as particle 1, particle j_1 as particle 2, ..., particle j_m as particle (m+1). Since there are N possibilities for choosing j, (N-1) for choosing j_1, ... (N-m) for choosing j_m, the summation over $j_1 j_2 \ldots j_m$ produces a factor (N-1)(N-2).. ..(N-m). Using this in (2.6) one gets:

$$F_k(t) = \sum_{m=1}^{N} \frac{N(N-1)(N-2)\ldots(N-m+1)}{N(m-1)!} < \sum_{i=1}^{N} \exp(-i\vec{k}\cdot\vec{r}_i) U_t(12..m)$$

$$\exp(i\vec{k}\cdot\vec{r}_1)>$$

$$= \sum_{m=1}^{N} \frac{N(N-1)(N-2)\ldots(N-m+1)}{Nm!} < \sum_{i=1}^{N} \exp(-i\vec{k}\cdot\vec{r}_i) U_t(12..m)$$

$$\sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j)> \qquad (2.7)$$

The first term of this expansion corresponds with the free streaming of particle 1 in the given time t. The other terms describe the trajectories of particle 1 in phase space resulting from dynamical interactions with the particles 2..m. Thus the particles (12..m) form an independent dynamical cluster and the motion of these particles is wholly determined by their mutual interactions. From (2.7) one sees that there is only a dynamical correlation at time t=0 and a time t later between the particles i and j as i belongs to the set (12..m). This suggests to split $F_k(t)$ in two terms $F_k^A(t)$ and $F_k^B(t)$; $F_k^A(t)$ represents mainly the dynamical correlations, $F_k^B(t)$ also the statistical correlations; they are given by the following expressions:

$$F_k^A(t) = \sum_{m=1}^{N} \frac{N(N-1)(N-2)\ldots(N-m+1)}{Nm!} < \sum_{i=1}^{m} \exp(-i\vec{k}\cdot\vec{r}_i) U_t(12..m)$$

$$\sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j)>$$

and (2.8)

$$F_k^B(t) = \sum_{m=1}^{N} \frac{N(N-1)(N-2)\ldots(N-m+1)}{Nm!} < \sum_{i=m+1}^{N} \exp(-i\vec{k}\cdot\vec{r}_i) U_t(12..m)$$

$$\sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j)>$$

Writing out the canonical ensemble average one arrives at:

$$F_k^A(t) = \sum_{m=1}^{N} \frac{N(N-1)(N-2)..(N-m+1)}{Nm!} \int d\Gamma\, \phi(p_1)..\phi(p_N)$$

$$Q_N^{-1} \exp(-\beta\Phi(\vec{r}_1..\vec{r}_N)) \sum_{i=1}^{m} \exp(-i\vec{k}\cdot\vec{r}_i) U_t(12..m)$$

$$\sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j) \qquad (2.9)$$

where $\phi(p_i)$ is the normalized Boltzmann distribution (1.4), Q_N the configuration integral (1.7) and $\Phi(\vec{r}_1..\vec{r}_N)$ the potential energy (1.6). The integrations over $\vec{p}_{m+1}...\vec{p}_N$ in (2.9) can immediately be carried out. It is also possible to do the integrations over $\vec{r}_{m+1}...\vec{r}_N$ formally, resulting in a m-particle static correlation function $g(\vec{r}_1\vec{r}_2..\vec{r}_m)$, defined in (1.5). After doing this one gets for $F_k^A(t)$:

$$F_k^A(t) = N^{-1} \sum_{m=1}^{N} \frac{1}{m!} \int d\vec{p}_1..d\vec{p}_m d\vec{r}_1..d\vec{r}_m \phi(p_1)..\phi(p_m) n^m g(\vec{r}_1..\vec{r}_m)$$

$$\sum_{i=1}^{m} \exp(-i\vec{k}\cdot\vec{r}_i) U_t(12..m) \sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j)$$

This can also be written as:

$$F_k^A(t) = N^{-1} \sum_{m=1}^{N} \frac{1}{m!} < \sum_{i=1}^{m} \exp(-i\vec{k}\cdot\vec{r}_i) U_t(1..m) \sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j) >_m \qquad (2.10)$$

where $<...>_m$ means an averaging over all possible m-particle configurations:

$$<f(\vec{p}_1..\vec{p}_m;\vec{r}_1..\vec{r}_m)>_m = \int d\vec{p}_1..d\vec{p}_m d\vec{r}_1..d\vec{r}_m \phi(p_1)..\phi(p_m)$$

$$n^m g(\vec{r}_1..\vec{r}_m) f(\vec{p}_1..\vec{p}_m;\vec{r}_1..\vec{r}_m) \qquad (2.11)$$

Expression (2.10) shows that there exists not only a dynamical correlation between the particles i and j but via the m-particle equilibrium correlation function $g(\vec{r}_1..\vec{r}_m)$ also a static correlation.

Returning to the "static part" $F_k^B(t)$ (2.8), we see that we have here to do with the particles i that are not dynamically correlated with the particles j so the summation over i runs from m+1 to N. Taking for particle i particle m+1 the summation over i produces only a factor (N-m):

$$F_k^B(t) = \sum_{m=1}^{N} \frac{(N-1)(N-2)..(N-m)}{m!} \langle \exp(-i\vec{k}.\vec{r}_{m+1}) U_t(1..m) \sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j) \rangle$$

In the same way as is done for $F_k^A(t)$ the integrations over $\vec{p}_{m+2}..\vec{p}_N$ and $\vec{r}_{m+2}..\vec{r}_N$ can be carried out; the result is:

$$F_k^B(t) = N^{-1} \sum_{m=1}^{N} \frac{1}{m!} \langle \exp(-i\vec{k}\cdot\vec{r}_{m+1}) U_t(12..m) \sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j) \rangle_{m+1} \tag{2.12}$$

The self part of the intermediate scattering function, $F_k^s(t)$, and the velocity autocorrelation function $C_D(t)$ are obtained in the same way. In this case the particles are always dynamically correlated so the "static" term disappears. For $F_k^s(t)$ one obtains the following expression:

$$F_k^s(t) = N^{-1} \sum_{m=1}^{N} \frac{1}{(m-1)!} \langle \exp(-i\vec{k}\cdot\vec{r}_1) U_t(1..m) \exp(i\vec{k}\cdot\vec{r}_1) \rangle_m \tag{2.13}$$

and for the velocity autocorrelation function:

$$C_D(t) = \frac{1}{3} \beta m N^{-1} \sum_{m=1}^{N} \frac{1}{(m-1)!} \langle \vec{v}_1 \cdot U_t(1..m) \vec{v}_1 \rangle_m \tag{2.14}$$

Finally we shall give an approximation for $F_k^B(t)$ in terms of $F_k^A(t)$. To do this we write for the equilibrium correlation function $g(\vec{r}_1..\vec{r}_{m+1})$:

$$n^{m+1} g(\vec{r}_1..\vec{r}_{m+1}) = n^m g(\vec{r}_1..\vec{r}_m)\, [n + + n \sum_{i=1}^{m} G(\vec{r}_{m+1}-\vec{r}_i) + \text{higher order correlations}] \qquad (2.15)$$

with G(r) = g(r)-1, the difference between the pair correlation function and its asymptotic value : 1 . We now make the following approximation: we restrict ourselves to the first two terms in the square brackets of (2.15). Thus we are considering the case that particle m+1 is either not correlated at all with the particles (1..m) or only correlated via a two particle correlation. Substitution of this approximated $g(\vec{r}_1..\vec{r}_{m+1})$ in (2.12) yields:

$$F_k^B(t) \simeq N^{-1} \sum_{m=1}^{N} \frac{1}{m!} \int d\vec{p}_1..d\vec{p}_{m+1} d\vec{r}_1..d\vec{r}_{m+1} \phi(p_1)..\phi(p_{m+1}) \, n^{m+1} g(\vec{r}_1..\vec{r}_m)[1+\sum_{i=1}^{m} G(\vec{r}_{m+1}-\vec{r}_i)] \, \exp(-i\vec{k}\cdot\vec{r}_{m+1}) U_t(1..m) \sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j) \qquad (2.16)$$

The integration over $\vec{p}_{m+1}$ gives 1 and for the integration over $\vec{r}_{m+1}$ one finds for k≠0:

$$\int d\vec{r}_{m+1} [1+\sum_{i=1}^{m} G(\vec{r}_{m+1}-\vec{r}_i)] \exp(-i\vec{k}\cdot\vec{r}_{m+1}) = \tilde{G}(k) \sum_{i=1}^{m} \exp(-i\vec{k}\cdot\vec{r}_i)$$

where $\tilde{G}(k)$ is the fourier transform of G(r). Inserting this in (2.16) one gets:

$$F_k^B(t) \simeq n\tilde{G}(k) N^{-1} \sum_{m=1}^{N} \frac{1}{m!} < \sum_{i=1}^{m} \exp(-i\vec{k}\cdot\vec{r}_i) U_t(1..m) \sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j) >_m = n\tilde{G}(k) F_k^A(t) \qquad (2.17)$$

where use has been made of (2.10). Adding together $F_k^A(t)$ and $F_k^B(t)$ one finds with (1.9):

$$F_k(t) \simeq [1+n\tilde{G}(k)]F_k^A(t) = S(k)F_k^A(t)$$

$$= S(k)N^{-1} \sum_{m=1}^{N} \frac{1}{m!} < \sum_{i=1}^{m} \exp(-i\vec{k}\cdot\vec{r}_i)U_t(1..m)$$

$$\sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j)>_m \qquad (2.18)$$

where S(k) is the structure factor. So it is in this approximation sufficient to calculate $F_k^A(t)$.

The results obtained in this section are listed together in table II.

Table II.

$$F_k(t) = F_k^A(t)+F_k^B(t) \simeq S(k)F_k^A(t)$$

$$F_k^A(t) = N^{-1} \sum_{m=1}^{N} \frac{1}{m!} < \sum_{i=1}^{m} \exp(-i\vec{k}\cdot\vec{r}_i)U_t(1..m) \sum_{j=1}^{m} \exp(i\vec{k}\cdot\vec{r}_j)>_m$$

$$F_k^B(t) = N^{-1} \sum_{m=1}^{N} \frac{1}{m!} <\exp(-i\vec{k}\cdot\vec{r}_{m+1})U_t(1..m) \sum_{j=1}^{m} \exp(i\vec{k}.\vec{r}_j)>_{m+1}$$

$$\simeq n\tilde{G}(k)F_k^A(t)$$

$$F_k^s(t) = N^{-1} \sum_{m=1}^{N} \frac{1}{(m-1)!} <\exp(-i\vec{k}\cdot\vec{r}_1)U_t(1..m)\exp(i\vec{k}\cdot\vec{r}_1)>_m$$

$$C_D(t) = \frac{1}{3} \beta mN^{-1} \sum_{m=1}^{N} \frac{1}{(m-1)!} <\vec{v}_1\cdot U_t(1..m)\vec{v}_1>_m$$

The Ursell expansion of the intermediate scattering functions $F_k(t)$ and $F_k^s(t)$ and of the velocity autocorrelation function $C_D(t)$.

2.3 THE TWO PARTICLE TERM

We shall now work out in detail the first two terms in the Ursell expansion of the correlation functions. The m = 1 term in (2.18), that represents the ideal gas, can be calculated exactly. Calling this term $F_k^{(1)}(t)$ we find with (2.18) and (2.11):

$$F_k^{(1)}(t)=N^{-1}S(k)\int d\vec{p}_1 d\vec{r}_1 \phi(p_1) n g(\vec{r}_1)\exp(-i\vec{k}\cdot\vec{r}_1)U_t(1)\exp(i\vec{k}\cdot\vec{r}_1) \tag{2.19}$$

$U_t(1)$ generates the free streaming of particle 1, so

$$U_t(1)\exp(i\vec{k}\cdot\vec{r}_1)=S_t^o(1)\exp(i\vec{k}\cdot\vec{r}_1)=\exp(i\vec{k}\cdot(\vec{r}_1+\vec{p}_1 t/m))$$

Inserting this in (2.19) and noticing that $g(\vec{r}_1) = 1$, for the intermediate scattering function of the ideal gas immediately is found:

$$F_k^{(1)}(t) = S(k)\exp(-k^2t^2/2\beta m) \tag{2.20}$$

In the same way we get for the free streaming part of the self function with (2.13):

$$F_k^{s(1)}(t) = \exp(-k^2t^2/2\beta m) \tag{2.21}$$

and with (2.14) for the velocity autocorrelation function:

$$C_D^{(1)}(t) = 1 \tag{2.22}$$

Because we are only interested in the deviations from the ideal gas behaviour we see that only the terms with $m \geq 2$ are of importance. From (1.32), (2.13), (2.18), (2.20) and (2.21) we find for the deviations $\varepsilon_k(t)$ and $\varepsilon_k^s(t)$ the following expressions:

$$\varepsilon_k(t) = N^{-1}\sum_{m=2}^{N}\frac{1}{m!}\langle\sum_{i=1}^{m}\exp(-i\vec{k}\cdot\vec{r}_i)U_t(1..m)\sum_{j=1}^{m}\exp(i\vec{k}\cdot\vec{r}_j)\rangle_m$$

and (2.23)

$$\varepsilon_k^s(t) = N^{-1}\sum_{m=2}^{N}\frac{1}{(m-1)!}\langle\exp(-i\vec{k}\cdot\vec{r}_1)U_t(1..m)\exp(i\vec{k}\cdot\vec{r}_1)\rangle_m$$

Note that the expression for $\varepsilon_k(t)$ simplifies due to the approximation (2.17).

For the short time behaviour of the correlation functions of a low density system one expects, as will be discussed later in this section, that the two particle collisions (terms with m=2) play a dominant role. Therefore we shall restrict ourselves in the following to the terms with m=2. The deviations will in this approximation be indicated by $\varepsilon_k^{(2)}(t)$ resp. $\varepsilon_k^{s(2)}(t)$. From (2.23) one finds for $\varepsilon_k^{(2)}(t)$:

$$\varepsilon_k^{(2)}(t) = \frac{1}{2}n^2N^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(\vec{r}_1\vec{r}_2)$$

$$\{\exp(-i\vec{k}\cdot\vec{r}_1)+\exp(-i\vec{k}\cdot\vec{r}_2)\}U_t(12)\{\exp(i\vec{k}\cdot\vec{r}_1)+\exp(i\vec{k}\cdot\vec{r}_2)\} \tag{2.24}$$

To carry out the integrations it is useful to split the motion of the two particles in their center-of-mass motion and their relative motion. So, instead of considering two particles of mass m with momenta $\vec{p}_1,\vec{p}_2$ and positions $\vec{r}_1,\vec{r}_2$ we look at a "center-of-mass particle" with mass 2m, momentum $\vec{P}$ and position $\vec{R}$ and a "relative particle" with the reduced mass m/2, momentum $\vec{p}$ and position $\vec{r}$. Thus we make the following transformation:

$$\begin{aligned} \vec{p}_1+\vec{p}_2 &= \vec{P} \qquad & \vec{r}_1+\vec{r}_2 &= 2\vec{R} \\ \vec{p}_1-\vec{p}_2 &= 2\vec{p} \qquad & \vec{r}_1-\vec{r}_2 &= \vec{r} \end{aligned} \tag{2.25}$$

When one keeps in mind that the pair correlation function in gases only depends on the relative distance of the both particles so that $g(\vec{r}_1\vec{r}_2) = g(r)$, and that

$$\phi(p_1)\phi(p_2) = \varphi(p)\Phi(P)$$

with

$$\varphi(p) = (\beta/\pi m)^{3/2}\exp(-\beta p^2/m) \tag{2.26}$$

and

$$\Phi(P) = (\beta/4\pi m)^{3/2}\exp(-\beta P^2/4m)$$

one finds for $\varepsilon_k^{(2)}(t)$:

$$\varepsilon_k^{(2)}(t) = \frac{1}{2} n^2 N^{-1} \int d\vec{p}d\vec{P}d\vec{r}d\vec{R}\varphi(p)\Phi(P)g(r)\exp(-i\vec{k}\cdot\vec{R})$$

$$\{\exp(i\vec{k}\cdot\vec{r}/2)+\exp(-i\vec{k}\cdot\vec{r}/2)\}U_t(12)\exp(i\vec{k}\cdot\vec{R})$$

$$\{\exp(i\vec{k}\cdot\vec{r}/2)+\exp(-i\vec{k}\cdot\vec{r}/2)\} \qquad (2.27)$$

Because the pair potential depends only on the relative distance of the particles the center of mass is streaming freely so it is possible to write for the Ursell operator $U_t(12)$:

$$U_t(12) = S_t^o(\vec{P}\vec{R})U_t(\vec{p}\vec{r})$$

where $S_t^o(\vec{P}\vec{R})$ is the free streaming operator for the "center of mass particle" with mass 2m while $U_t(\vec{p}\vec{r})$ is the difference of the streaming operator with interaction and that without interaction, both with respect to the relative motion. Thus one finds:

$$U_t(12)\exp(i\vec{k}\cdot\vec{R})\exp(i\vec{k}\cdot\vec{r}/2)=S_t^o(\vec{P}\vec{R})\exp(i\vec{k}\cdot\vec{R})U_t(\vec{p}\vec{r})\exp(i\vec{k}\cdot\vec{r}/2)$$

$$= \exp(i\vec{k}\cdot(\vec{R}+\vec{P}t/2m))U_t(\vec{p}\vec{r})\exp(i\vec{k}\cdot\vec{r}/2) \qquad (2.28)$$

Insertion of this expression in (2.27) yields:

$$\varepsilon_k^{(2)}(t) = \frac{1}{2} n^2 N^{-1} \int d\vec{p}d\vec{P}d\vec{r}d\vec{R}\varphi(p)\Phi(P)g(r)\exp(i\vec{k}\cdot\vec{P}t/2m)$$

$$\{\exp(i\vec{k}\cdot\vec{r}/2)+\exp(-i\vec{k}\cdot\vec{r}/2)\}U_t(\vec{p}\vec{r})\{\exp(i\vec{k}\cdot\vec{r}/2)+\exp(-i\vec{k}\cdot\vec{r}/2)\}$$

Now one can integrate over the center of mass momenta $\vec{P}$ and coordinates $\vec{R}$, resulting in:

$$\varepsilon_k^{(2)}(t) = \frac{1}{2} n \exp(-k^2t^2/4\beta m) \int d\vec{p}d\vec{r}\varphi(p)g(r)$$

$$\{\exp(i\vec{k}\cdot\vec{r}/2)+\exp(-i\vec{k}\cdot\vec{r}/2)\}$$

$$U_t(\vec{p}\vec{r})\{\exp(i\vec{k}\cdot\vec{r}/2)+\exp(-i\vec{k}\cdot\vec{r}/2)\}$$

The action of $U_t(\vec{p}\vec{r})$ on $\vec{r}$ gives the difference between the real trajectory $\vec{r}(t)$ and the free streaming $\vec{r}+2\vec{p}t/m$, so

$$U_t(\vec{p}\vec{r})\exp(i\vec{k}\cdot\vec{r}/2) = \exp(i\vec{k}\cdot\vec{r}(t)/2)-\exp(i\vec{k}\cdot(\vec{r}+2\vec{p}t/m))/2$$

Thus $\varepsilon_k^{(2)}(t)$ becomes:

$$\varepsilon_k^{(2)}(t) = \frac{1}{2} n \exp(-k^2t^2/4\beta m) \int d\vec{p}d\vec{r}\varphi(p)g(r)$$

$$\{\exp(i\vec{k}\cdot\vec{r}/2)+\exp(-i\vec{k}\cdot\vec{r}/2)\}$$

$$\{\exp(i\vec{k}\cdot\vec{r}(t)/2)+\exp(-i\vec{k}\cdot\vec{r}(t)/2)-\exp(i\vec{k}\cdot(\vec{r}/2+\vec{p}t/m))$$

$$- \exp(-i\vec{k}\cdot(\vec{r}/2+\vec{p}t/m))\} \qquad (2.29)$$

The intermediate scattering function of an isotropic system can only depend on the magnitude of $\vec{k}$, so it is allowed to average over the direction $\hat{k}$ of $\vec{k}$. This has the advantage that one gets rid of an additional direction (that of $\vec{k}$) in the integrand of (2.29). If $\vec{a}$ is an arbitrary vector then one finds for such an average:

$$\int d\hat{k} \exp(i\vec{k}\cdot\vec{a}) / \int d\hat{k} = j_o(k|\vec{a}|) \qquad (2.30)$$

with $j_o(x) = x^{-1}\sin x$, the zeroth order spherical Bessel function and $k = |\vec{k}|$.

Averaging the right hand side of (2.29) in this way over $\hat{k}$

gives the following expression:

$$\varepsilon_k^{(2)}(t) = n \exp(-k^2t^2/4\beta m) \int d\vec{p}d\vec{r}\varphi(p)g(r)$$

$$[j_o(k|\vec{r}+\vec{r}(t)|/2)+j_o(k|\vec{r}-\vec{r}(t)|/2)- \tag{2.31}$$

$$-j_o(kpt/m)-j_o(k|\vec{r}+\vec{p}t/m|)]$$

In the case of the self part of the intermediate scattering function the calculation goes analogously. We shall give here only the result:

$$\varepsilon_k^{s(2)}(t) = n \exp(-k^2t^2/4\beta m) \int d\vec{p}d\vec{r}\varphi(p)g(r)$$

$$[j_o(k|\vec{r}-\vec{r}(t)|/2)-j_o(kpt/m)] \tag{2.32}$$

The order of magnitude of the deviations (2.31) and (2.32) is found by considering the expressions between the square brackets; if the particles are free streaming these terms have the numerical value 0, while, if the particles are colliding, they can roughly be approximated by the value 1. The integrals yield then precisely the volume in phase space containing the particles that within a time t are going to collide; the volume of this collision cylinder is $\pi\sigma^2vt$ with σ the diameter of the particles and v the thermal velocity. Thus a crude estimate of the deviations $\varepsilon_k^{(2)}(t)$ and $\varepsilon_k^{s(2)}(t)$ is, apart from a numerical factor, $\pi n\sigma^2vt = t/\tau$ where τ is the mean free time. One sees that the restriction to the two particle terms is justified for low densities and for times small compared with the mean free time.

Finally one finds from (2.14) for the two particle term of the velocity autocorrelation function:

$$C_D^{(2)}(t) = \frac{1}{3}\beta(Nm)^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)$$

$$n^2 g(\vec{r}_1\vec{r}_2)\vec{p}_1 \cdot U_t(12)\vec{p}_1 \qquad (2.33)$$

Making again the transformation to the relative and the center of mass coordinates of the both particles and noting that for the center of mass motion holds

$$U_t(12)\vec{P} = 0$$

while for the relative motion

$$U_t(12)\vec{p} = \vec{p}(t)-\vec{p}$$

one gets immediately for $C_D^{(2)}(t)$:

$$C_D^{(2)}(t) = \frac{1}{3}\beta n^2(Nm)^{-1}\int d\vec{p}d\vec{P}d\vec{r}d\vec{R}\varphi(p)\Phi(P)g(r)$$

$$(\vec{P}/2+\vec{p})\cdot(\vec{p}(t)-\vec{p})$$

The integrations over the center of mass momenta and coordinates are very easy and yield:

$$C_D^{(2)}(t) = \frac{1}{3}\beta n/m\int d\vec{p}d\vec{r}\varphi(p)g(r)(\vec{p}\cdot\vec{p}(t)-p^2) \qquad (2.34)$$

The two particle terms of the deviations of the intermediate scattering functions and of the velocity autocorrelation function are put together in table III.

Table III.

$$\varepsilon_k^{(2)}(t) = n\,\exp(-k^2t^2/4\beta m)\int d\vec{p}d\vec{r}\varphi(p)g(r)[\,j_o(k|\vec{r}+\vec{r}(t)|/2)$$

$$+j_o(k|\vec{r}-\vec{r}(t)|/2)-j_o(kpt/m)-j_o(k|\vec{r}+\vec{p}t/m|)]$$

$$\varepsilon_k^{s(2)}(t) = n\,\exp(-k^2t^2/4\beta m)\int d\vec{p}d\vec{r}\varphi(p)g(r)[\,j_o(k|\vec{r}-\vec{r}(t)|/2)$$

$$-j_o(kpt/m)]$$

$$C_D^{(2)}(t) = \frac{1}{3}\,\beta n/m\int d\vec{p}d\vec{r}\varphi(p)g(r)(\vec{p}\cdot\vec{p}(t)-p^2)$$

Two particle collision terms in the Ursell expansion of the deviations of $F_k(t)$, $F_k^s(t)$ and $C_D(t)$ from their ideal gas values.

2.4 THE MOMENTS OF THE TWO PARTICLE TERMS

For a good short time theory its moments have to correspond with the in Ch. 1.3 given exact values. It is therefore interesting to see what the moments are of the two particle terms in the Ursell expansion. These moments will be indicated by a superscript u. Let us begin with the deviation of the intermediate scattering function, given by (2.24):

$$\varepsilon_k^{(2)}(t) = \frac{1}{2}n^2N^{-1}\int d\vec{p}_1d\vec{p}_2d\vec{r}_1d\vec{r}_2\phi(p_1)\phi(p_2)g(r_{12})$$

$$\{\exp(-i\vec{k}\cdot\vec{r}_1)+\exp(-i\vec{k}\cdot\vec{r}_2)\}U_t(12)\{\exp(i\vec{k}\cdot\vec{r}_1)+\exp(i\vec{k}\cdot\vec{r}_2)\} \tag{2.24}$$

The coefficients of the successive powers of the time t are found by expanding the Ursell operator $U_t(12)$ in the following way, using (2.2):

$$U_t(12) = \exp(tL(12))-\exp(tL_o(12))$$

$$= \sum_{n=0}^{\infty} \frac{t^n}{n!} [\{L(12)\}^n-\{L_o(12)\}^n] \qquad (2.35)$$

After substituting this in (2.24) the coefficients of the zeroth and first power of t are immediately found to be zero. The calculation of the coefficient of t^2 is more complicated and is given in detail in appendix C. The results for the first moments are:

$$M_o^u = S(k) = M_o$$

$$M_1^u = 0 = M_1$$

$$M_2^u = (-k^2S(k)/\beta m)+4\pi(nkS(k)/m)\int_o^\infty r^2g(r)j_1(kr)\varphi'(r)dr \qquad (2.36)$$

with

$$j_1(kr) = (kr)^{-2}\sin kr-(kr)^{-1}\cos kr,$$

the first order spherical Bessel function. The fourth moment is not worked out but it is clear that it will not yield the exact value, since already $M_2^u \neq M_2$ (see (1.39)).

Of course it is also possible to make a time expansion of the deviation $\varepsilon_k(t)$. Writing

$$\varepsilon_k(t) = \sum_{n=0}^{\infty} \varepsilon_n \, t^n/n!$$

one sees with (1.32) and (1.37) immediately that the first non zero moment of $\varepsilon_k(t)$ is the second moment:

$$\varepsilon_2 = k^2/\beta m + M_2(k)/S(k)$$

Substituting $M_2(k)$ from (1.39) one finds for the exact second moment of $\varepsilon_k(t)$:

$$\varepsilon_2 = k^2(\beta m)^{-1}\,[\,1-1/S(k)]$$

while the Ursell second moment is:

$$\varepsilon_2^u = k^2/\beta m + M_2^u(k)/S(k)$$

with $M_2^u(k)$ given in (2.36).

To see how large the difference is between the exact second moment and the Ursell second moment, both moments are calculated for the case of a Lennard-Jones (12,6) potential (fig. 1). One

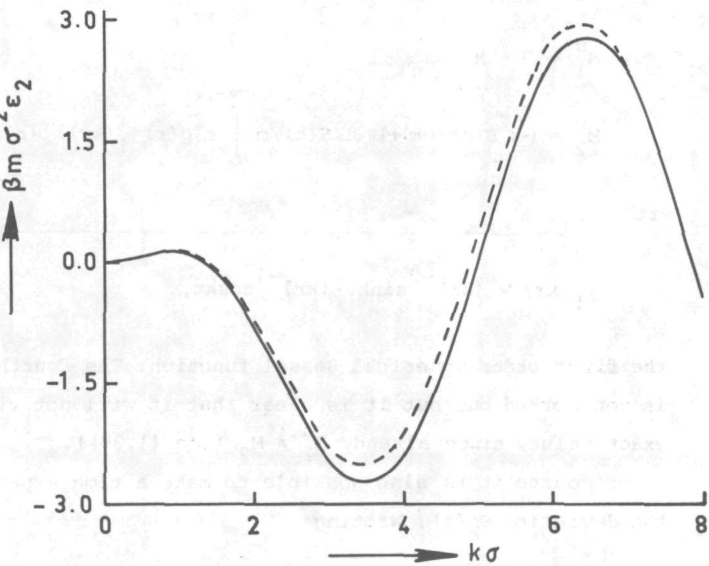


Fig. 1 Comparison of the exact second moment ε_2 (full line) with the Ursell second moment ε_2^u (dashed line) for a Lennard-Jones (12,6) potential ($\varphi(r) = 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]$). The density $n\sigma^3 = 0.1$, the temperature $k_BT/\varepsilon = 1.5$.

observes that the discrepancy is small. The differences between the exact and Ursell values for the second moment are completely due to the approximation (2.16); expansion of the two particle terms in the original expressions of $F_k^A(t)$ and

$F_k^B(t)$, (2.10) and (2.12), leads to the exact second moment.

Because in the derivation of the two particle term (2.32) of the self part of the intermediate scattering function no approximation is made, one expects that at least its second moment agrees with the exact value. The detailed calculation is again carried out in appendix C; the results for the first four moments are:

$$M_o^{s,u} = 1 = M_o^s$$

$$M_1^{s,u} = 0 = M_1^s$$

$$M_2^{s,u} = -k^2/\beta m = M_2^s \qquad (2.37)$$

$$M_3^{s,u} = 0 = M_3$$

$$M_4^{s,u} = 3k^4(\beta m)^{-2} + nk^2 m^{-2} \int d\vec{r} g(r) [\tfrac{4}{3} \beta^{-1} \vec{\nabla}^2 \varphi(r) - (d\varphi/dr)^2]$$

Indeed the second moment of the Ursell expansion of the self function is equal to the exact second moment. However, here appears a difference between the Ursell fourth moment and the exact fourth moment.

The moments of the two particle term of the velocity auto correlation function are also derived in appendix C. The first moments agree completely with the corresponding exact moments C_o, C_1 and C_2 (1.41).

2.5 THE SECOND DERIVATIVE EXPANSION

The last three sections were concerned with the Ursell expansion of the intermediate scattering functions and the velocity autocorrelation function. For instance $F_k(t)$ could with (1.12), (1.13) and (1.28) be written as:

$$F_k(t) = N^{-1} < \sum_{i=1}^{N} \exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL(1..N)) \sum_{j=1}^{N} \exp(i\vec{k}\cdot\vec{r}_j)>$$
$$= \int d\Gamma\rho(\Gamma) N^{-1} \sum_{i=1}^{N} \exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL) \sum_{j=1}^{N} \exp(i\vec{k}\cdot\vec{r}_j) \tag{2.38}$$

where $\rho(\Gamma) = \exp(-\beta H(\Gamma))/\int d\Gamma \exp(-\beta H(\Gamma))$ is the phase space density. The next step was the Ursell expansion (2.1) of the streaming operator exp(tL). Each term contained an Ursell operator $U_t(1..m)$. This gave rise to a splitting of each term into two parts: one part contained the particles i that belonged to the set of colliding particles 1,2..m, the other part contained the remaining particles. We called these parts $F_k^A(t)$ resp. $F_k^B(t)$ (2.8). The m'th term in $F_k^B(t)$ was more difficult to calculate as the corresponding term in $F_k^A(t)$ because the B-term was an average over m+1 particles (2.12) whereas the A-term was only a m-particle average (2.10). Therefore the B-terms were with the approximation (2.16) reduced to a much simpler form. But this had the undesirable consequence that the second moment (2.36) in the two particle collisions term did not agree with the exact second moment.

Therefore the question rises if there exists another expansion where the splitting in A- and B-terms does not occur. Such an expansion will be given here and is inspired on the work of Rao (1974).

Starting point is not $F_k(t)$ itself but its first derivative:

$$\frac{\partial F_k(t)}{\partial t} = N^{-1}<\sum_i \exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL)L \sum_j \exp(i\vec{k}\cdot\vec{r}_j)>$$
$$= N^{-1}<\sum_i \exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL)\sum_j (i\vec{k}\cdot\vec{p}_j/m)\exp(i\vec{k}\cdot\vec{r}_j)>$$
$$= N^{-1}\int d\Gamma\rho(\Gamma)\sum_i \exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL)\sum_j (i\vec{k}\cdot\vec{p}_j/m)\exp(i\vec{k}\cdot\vec{r}_j) \tag{2.39}$$

whereafter an integration follows over t to obtain $F_k(t)$. In the straightforward Ursell expansion of this first derivative again the A- and B-terms are present leading to approximation (2.16). However, because the Liouville operator L(1..N) and the Hamilton function $H(\Gamma)$ commute with each other, (2.39) may also be written as:

$$\frac{\partial F_k(t)}{\partial t} = N^{-1}\int d\Gamma \sum_i \exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL)\sum_j(i\vec{k}\cdot\vec{p}_j/m)\exp(i\vec{k}\cdot\vec{r}_j)\rho(\Gamma) \tag{2.40}$$

If one substitutes in (2.40) for the streaming operator exp(tL) the Ursell expansion (2.1) one gets an expansion similar to that of Rao. After working out the two particle term it appears that the splitting in A- and B-terms is absent and furthermore that the second and fourth moment are in agreement with the corresponding exact values. Because Rao derives his expansion in the frequency domain his zeroth moment is not the same as the exact zeroth moment. What we consider as another drawback of this approach is that the Ursell operators work also on the phase space density.

Another possibility is to take the second derivative of $F_k(t)$ as starting point. We will show in the rest of this chapter that in this method the B-terms are also absent and that the first four moments agree with the corresponding exact values.

The second derivative of $F_k(t)$ follows from (2.38) as:

$$\frac{\partial^2 F_k(t)}{\partial t^2} = N^{-1}\int d\Gamma\rho(\Gamma)\sum_i \exp(-i\vec{k}\cdot\vec{r}_i)\,L\exp(tL)\,L\sum_j \exp(i\vec{k}\cdot\vec{r}_j)$$

Because for a non singular interaction the Liouville operator is antihermitian (1.18), this can be written as:

$$\frac{\partial^2 F_k(t)}{\partial t^2} = N^{-1}\int d\Gamma\rho(\Gamma)[-L\sum_i \exp(-i\vec{k}\cdot\vec{r}_i)]\exp(tL)\,L\sum_j \exp(i\vec{k}\cdot\vec{r}_j)$$

$$= N^{-1}\int d\Gamma\,\rho(\Gamma)\sum_i(i\vec{k}\cdot\vec{p}_i/m)\exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL)\sum_j(i\vec{k}\cdot\vec{p}_j/m)\exp(i\vec{k}\cdot\vec{r}_j) \tag{2.41}$$

In an analogous way the second derivative of the self part of the intermediate scattering function is obtained as:

$$\frac{\partial^2 F_k^s(t)}{\partial t^2} = N^{-1}\int d\Gamma\rho(\Gamma)\sum_i (i\vec{k}\cdot\vec{p}_i/m)\exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL)(i\vec{k}\cdot\vec{p}_i/m)$$

$$\exp(i\vec{k}\cdot\vec{r}_i) \qquad (2.42)$$

If we now substitute in (2.41) and (2.42) for the streaming operator exp(tL) the Ursell expansion (2.1) we get what we shall call the second derivative expansion:

$$\frac{\partial^2 F_k(t)}{\partial t^2} = N^{-1}\int d\Gamma\rho(\Gamma)\sum_i (i\vec{k}\cdot\vec{p}_i/m)\exp(-i\vec{k}\cdot\vec{r}_i)[U_t(1)\ldots U_t(N)+$$

$$+\sum_{\{j_1j_2\}} U_t(j_1j_2)U_t(1)..U_t(j_1-1)U_t(j_1+1)..$$

$$..U_t(j_2-1)U_t(j_2+1)..U_t(N)+..]\sum_j(i\vec{k}\cdot\vec{p}_j/m)\exp(i\vec{k}\cdot\vec{r}_j)$$

$$(2.43)$$

and an analogous expression for the self function:

$$\frac{\partial^2 F_k^s(t)}{\partial t^2} = N^{-1}\int d\Gamma\rho(\Gamma)\sum_i (i\vec{k}\cdot\vec{p}_i/m)\exp(-i\vec{k}\cdot\vec{r}_i)[U_t(1)..U_t(N)+$$

$$+\sum_{\{j_1j_2\}} U_t(j_1j_2)U_t(1)..U_t(j_1-1)U_t(j_1+1)..$$

$$..U_t(j_2-1)U_t(j_2+1)..U_t(N)+..](i\vec{k}\cdot\vec{p}_i/m)\exp(i\vec{k}\cdot\vec{r}_i)$$

$$(2.44)$$

If the second derivatives are known, the intermediate scattering functions can easily be obtained from:

$$F_k(t) = F_k(0) + \int_o^t dt' \int_o^{t'} dt'' \frac{\partial^2 F_k(t'')}{\partial t''^2}$$

and (2.45)

$$F_k^s(t) = F_k^s(0) + \int_o^t dt' \int_o^{t'} dt'' \frac{\partial^2 F_k^s(t'')}{\partial t''^2}$$

where $F_k(0) = S(k)$ and $F_k^s(0) = 1$. In the following section we shall derive detailed expressions for the two particle terms of (2.43) and (2.44).

2.6 THE FREE STREAMING AND TWO PARTICLE TERMS IN THE SECOND DERIVATIVE EXPANSION

The free streaming part of the second derivative of the intermediate scattering function follows from (2.43) as:

$$\left(\frac{\partial^2 F_k(t)}{\partial t^2}\right)_1 = N^{-1}\int d\Gamma\rho(\Gamma)\sum_i(i\vec{k}\cdot\vec{p}_i/m)\exp(-i\vec{k}\cdot\vec{r}_i) \quad (2.46)$$
$$U_t(1)..U_t(N)\sum_j(i\vec{k}\cdot\vec{p}_j/m)\exp(i\vec{k}\cdot\vec{r}_j)$$

According to the definition of the free streaming operator $U_t(1)..U_t(N)$ we have to make in all quantities on the right of it the following substitution:

$$\vec{p}_j \rightarrow \vec{p}_j$$

$$\vec{r}_j \rightarrow \vec{r}_j+\vec{p}_j t/m$$

So (2.46) becomes:

$$\left(\frac{\partial^2 F_k(t)}{\partial t^2}\right)_1 = -N^{-1}\int d\Gamma\rho(\Gamma)\sum_i \vec{k}\cdot\vec{p}_i/m \exp(-i\vec{k}\cdot\vec{r}_i)\sum_j \vec{k}\cdot\vec{p}_j/m$$
$$\exp(i\vec{k}\cdot(\vec{r}_j+\vec{p}_j t/m))$$

Because the momentum integrations of $(\vec{k}\cdot\vec{p}_i/m)(\vec{k}\cdot\vec{p}_j/m)$ give a zero result for $i \neq j$ only the terms with $i = j$ survive. We can take particle i as particle 1, the summation over i produces only a factor N and thus holds:

$$\left(\frac{\partial^2 F_k(t)}{\partial t^2}\right)_1 = -\int d\vec{p}_1\phi(p_1)(\vec{k}\cdot\vec{p}_1/m)^2\exp(i\vec{k}\cdot\vec{p}_1 t/m)$$

The momentum integrations are elementary and yield:

$$\left(\frac{\partial^2 F_k(t)}{\partial t^2}\right)_1 = -k^2 m^{-2}(m/\beta - k^2 t^2/\beta^2)\exp(-k^2 t^2/2\beta m)$$

The double time integral in (2.45) becomes:

$$\int_0^t dt' \int_0^{t'} dt'' \left(\frac{\partial^2 F_k(t'')}{\partial t''^2}\right)_1 = \exp(-k^2 t^2/2\beta m) - 1 \qquad (2.47)$$

The self function is treated in exactly the same manner, leading to:

$$\int_0^t dt' \int_0^{t'} dt'' \left(\frac{\partial^2 F_k^s(t'')}{\partial t''^2}\right)_1 = \exp(-k^2 t^2/2\beta m) - 1 \qquad (2.48)$$

With (2.47) and (2.48) the expressions (2.45) for the intermediate scattering functions take the following form:

$$F_k(t) = S(k) - 1 + \exp(-k^2 t^2/2\beta m) + F_k^{(2)}(t) + ..$$

and (2.49)

$$F_k^s(t) = \exp(-k^2 t^2/2\beta m) + F_k^{s(2)}(t) + ..$$

where $F_k^{(2)}(t)$ and $F_k^{s(2)}(t)$ are the double time integrals of the two particle terms in (2.43) and (2.44).

$F_k^{(2)}(t)$ is given in detail by:

$$F_k^{(2)}(t) = \int_0^t dt' \int_0^{t'} dt'' N^{-1} \int d\Gamma \rho(\Gamma) \sum_i i\vec{k}\cdot\vec{p}_i/m \exp(-i\vec{k}\cdot\vec{r}_i) \sum_{\{j_1 j_2\}}$$

$$U_{t''}(j_1 j_2) U_{t''}(1) .. U_{t''}(j_1 - 1) U_{t''}(j_1 + 1) ..$$

$$.. U_{t''}(j_2 - 1) U_{t''}(j_2 + 1) .. U_{t''}(N) \sum_j i\vec{k}\cdot\vec{p}_j/m \exp(i\vec{k}\cdot\vec{r}_j)$$

(2.50)

Without loss of generality we can take particle i as particle 1. It is clear that j must be equal to one of the colliding particles j_1 or j_2 to give a non zero contribution. Then the product of free streaming operators $U_{t''}(1)..U_{t''}(N)$, in which $U_{t''}(j_1)$ and $U_{t''}(j_2)$ are absent, gives a factor 1 because it works on a function depending only on the particles j_1 and j_2. Furthermore $\langle i\vec{k}\cdot\vec{p}_1/m\rangle = 0$, thus the contributions of all pairs $(j_1 j_2)$ that do not contain particle 1 vanish. So we can take for the particles j_1 and j_2 the particles 1 and 2, the summation over all pairs $(j_1 j_2)$ produces a factor (N-1) and $F_k^{(2)}(t)$ becomes:

$$F_k^{(2)}(t) = -(N-1)\int_0^t dt\int_0^{t'} dt''\int d\Gamma\rho(\Gamma)\vec{k}\cdot\vec{p}_1/m\ \exp(-i\vec{k}\cdot\vec{r}_1)U_{t''}(12)$$
$$(\vec{k}\cdot\vec{p}_1/m\ \exp(i\vec{k}\cdot\vec{r}_1)+\vec{k}\cdot\vec{p}_2/m\ \exp(i\vec{k}\cdot\vec{r}_2)) \qquad (2.51)$$

One sees that because of the occurrence of $\vec{k}\cdot\vec{p}_i/m$ in (2.50), which averages to zero if i does not belong to the pair $(j_1 j_2)$, in this second derivative expansion no splitting in A- and B-terms takes place as in the case of the Ursell expansion. Therefore in this term of the present expansion no approximation at all is needed.

Using (1.5) the integrations over the variables $\vec{r}_3..\vec{r}_N$, $\vec{p}_3..\vec{p}_N$ in (2.51) can be done:

$$F_k^{(2)}(t) = -n^2N^{-1}\int_0^t dt'\int_0^{t'} dt''\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\vec{k}\cdot\vec{p}_1/m$$
$$\exp(-i\vec{k}\cdot\vec{r}_1)U_{t''}(12)(\vec{k}\cdot\vec{p}_1/m\ \exp(i\vec{k}\cdot\vec{r}_1)+\vec{k}\cdot\vec{p}_2/m\ \exp(i\vec{k}\cdot\vec{r}_2))$$
$$(2.52)$$

Remembering that (2.2):

$$U_t(12) = \exp(tL(12))-\exp(tL_o(12))$$

one can easily verify that

$$U_t(12)(\vec{k}\cdot\vec{p}_1/m \exp(i\vec{k}\cdot\vec{r}_1)+\vec{k}\cdot\vec{p}_2/m \exp(i\vec{k}\cdot\vec{r}_2))$$

$$= -i \frac{\partial}{\partial t} [U_t(12)(\exp(i\vec{k}\cdot\vec{r}_1)+\exp(i\vec{k}\cdot\vec{r}_2))]$$

and so the integration over t" in (2.52) yields the following result:

$$F_k^{(2)}(t) = in^2N^{-1}\int_o^t dt'\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\vec{k}\cdot\vec{p}_1/m$$
$$\exp(-i\vec{k}\cdot\vec{r}_1)U_{t'}(12)(\exp(i\vec{k}\cdot\vec{r}_1)+\exp(i\vec{k}\cdot\vec{r}_2)) \qquad (2.53)$$

We now introduce center of mass variables $\vec{P}$, $\vec{R}$ and relative variables $\vec{p}$, $\vec{r}$, defined in (2.25), and obtain, using (2.26) and (2.28), for $F_k^{(2)}(t)$:

$$F_k^{(2)}(t) = in^2N^{-1}\int_o^t dt'\int d\vec{p}d\vec{P}d\vec{r}d\vec{R}\Phi(P)\varphi(p)g(r)\vec{k}\cdot(\vec{P}/2+\vec{p})/m$$
$$\exp(-i\vec{k}\cdot\vec{r}/2)\exp(i\vec{k}\cdot\vec{P}t'/2m)[\exp(i\vec{k}\cdot\vec{r}(t')/2)+$$
$$+\exp(-i\vec{k}\cdot\vec{r}(t')/2)-\exp(i\vec{k}\cdot(\vec{r}+2\vec{p}t'/m)/2)$$
$$-\exp(-i\vec{k}\cdot(\vec{r}+2\vec{p}t'/m)/2)]$$

After doing the integrations over the center of mass variables $\vec{P}$ and $\vec{R}$ one gets:

$$F_k^{(2)}(t) = in\int_o^t dt'\exp(-k^2t'^2/4\beta m)\int d\vec{p}d\vec{r}\varphi(p)g(r)(\tfrac{1}{2}\, ik^2t'(\beta m)^{-1}+$$
$$+\vec{k}\cdot\vec{p}/m)\exp(-i\vec{k}\cdot\vec{r}/2)[\exp(i\vec{k}\cdot\vec{r}(t')/2)+\exp(-i\vec{k}\cdot\vec{r}(t')/2)$$
$$-\exp(i\vec{k}\cdot(\vec{r}+2\vec{p}t'/m)/2)-\exp(-i\vec{k}\cdot(\vec{r}+2\vec{p}t'/m)/2)] \qquad (2.54)$$

Because of isotropy $F_k^{(2)}(t)$ depends only on the magnitude of $\vec{k}$, so, to get rid of the vector $\vec{k}$, it is permitted to average

(2.54) over the direction $\hat{k}$ of $\vec{k}$. Using (2.30) and the relation

$$(4\pi)^{-1}\int d\hat{k}(\vec{k}\cdot\vec{b})\exp(i\vec{k}\cdot\vec{a}) = ik\ \hat{a}\cdot\vec{b}\ j_1(k|\vec{a}|) \tag{2.55}$$

with $j_1(k|\vec{a}|)$ the first order spherical Bessel function and $\vec{a}$ and $\vec{b}$ arbitrary vectors, we find finally for the two particle contribution:

$$F_k^{(2)}(t) = \frac{1}{2}nk^2\int_o^t dt'\exp(-k^2t'^2/4\beta m)\int d\vec{p}d\vec{r}\varphi(p)g(r)f_k(\vec{p}\vec{r};t') \tag{2.56}$$

with

$$f_k(\vec{p}\vec{r};t') = -(\beta m)^{-1}t'[j_o(k|\vec{r}+\vec{r}(t')|/2)+j_o(k|\vec{r}-\vec{r}(t')|/2)$$
$$-j_o(k|\vec{r}+\vec{p}t'/m|)-j_o(kpt'/m)] + 2\vec{p}/m\cdot[\frac{1}{2}(\vec{r}+\vec{r}(t'))$$
$$\frac{j_1(k|\vec{r}+\vec{r}(t')|/2)}{k|\vec{r}+\vec{r}(t')|/2} + \frac{1}{2}(\vec{r}-\vec{r}(t'))\ \frac{j_1(k|\vec{r}-\vec{r}(t')|/2)}{k|\vec{r}-\vec{r}(t')|/2} -$$
$$-(\vec{r}+\vec{p}t'/m)\ \frac{j_1(k|\vec{r}+\vec{p}t'/m|)}{k|\vec{r}+\vec{p}t'/m|} + \vec{p}t'/m\ \frac{j_1(kpt'/m)}{kpt'/m}] \tag{2.57}$$

The two particle term $F_k^{s(2)}(t)$ of the self part of the intermediate scattering function follows from (2.44) as:

$$F_k^{s(2)}(t) = \int_o^t dt'\int_o^{t'} dt''N^{-1}\int d\Gamma\rho(\Gamma)\sum_i i\vec{k}\cdot\vec{p}_i/m\exp(-i\vec{k}\cdot\vec{r}_i)\sum_{\{j_1j_2\}}$$
$$U_{t''}(j_1j_2)U_{t''}(1)..U_{t''}(j_1-1)U_{t''}(j_1+1)..U_{t''}(j_2-1)U_{t''}(j_2+1)..$$
$$..U_{t''}(N)i\vec{k}\cdot\vec{p}_i/m\exp(i\vec{k}\cdot\vec{r}_i)$$

The same procedure as was applied to $F_k^{(2)}(t)$ can for this self part be used; the result is:

$$F_k^{s(2)}(t) = \frac{1}{2}nk^2\int_o^t dt'\exp(-k^2t'^2/4\beta m)\int d\vec{p}d\vec{r}\varphi(p)g(r)f_k^s(\vec{p}\vec{r};t') \tag{2.58}$$

with

$$f_k^s(\vec{p}\vec{r};t') = -(\beta m)^{-1}t'[j_o(k|\vec{r}-\vec{r}(t')|/2)-j_o(kpt'/m)]+2\vec{p}/m\cdot$$

$$\cdot[\frac{1}{2}(\vec{r}-\vec{r}(t'))\frac{j_1(k|\vec{r}-\vec{r}(t')|/2)}{k|\vec{r}-\vec{r}(t')|/2}+\vec{p}t'/m\frac{j_1(kpt'/m)}{kpt'/m}] \tag{2.59}$$

Finally we shall denote how the deviations $\varepsilon_k^{(2)}(t)$ and $\varepsilon_k^{s(2)}(t)$ of the intermediate scattering functions from their ideal gas values can be expressed in $F_k^{(2)}(t)$ and $F_k^{s(2)}(t)$ as given in (2.56)-(2.59). From (1.32) and (2.49) it follows immediately that, as far as the two particle collisions are concerned:

$$\varepsilon_k^{(2)}(t) = (1-1/S(k))(1-\exp(-k^2t^2/2\beta m))+F_k^{(2)}(t)/S(k)$$

and (2.60)

$$\varepsilon_k^{s(2)}(t) = F_k^{s(2)}(t)$$

The results that were obtained in this section for the second derivative expansion are listed together in table IV.

It is now interesting to see if the moments in the second derivative expansion agree better with the exact moments than those of the Ursell expansion. For this purpose expression (2.53) is a suitable starting point. A time expansion of this two particle term can be found by substituting (2.35) for the Ursell operator $U_{t'}(12)$ in the same way as was done for the Ursell expansion. The calculation of the moments is carried out in appendix D. It appears that there is up to the fourth moment (coherent and incoherent) complete agreement with the exact moments (1.39) and (1.40).

We have thus made a considerable progress with respect to the straightforward Ursell expansion because on the one hand

Table IV

Intermediate scattering functions and deviations from their ideal gas values in the second derivative expansion.

Coherent intermediate scattering function

$$F_k(t) = S(k)-1+\exp(-k^2t^2/2\beta m)+F_k^{(2)}(t)$$

$$\varepsilon_k^{(2)}(t) = (1-1/S(k))(1-\exp(-k^2t^2/2\beta m))+F_k^{(2)}(t)/S(k)$$

$$F_k^{(2)}(t) = \frac{1}{2}nk^2\int_o^t dt'\exp(-k^2t'^2/4\beta m)\int d\vec{p}d\vec{r}\varphi(p)g(r)f_k(\vec{p}\vec{r};t')$$

$$f_k(\vec{p}\vec{r};t') = -(\beta m)^{-1}t'[j_o(k|\vec{r}+\vec{r}(t')|/2)+j_o(k|\vec{r}-\vec{r}(t')|/2)-$$

$$-j_o(k|\vec{r}+\vec{p}t'/m|)-j_o(kpt'/m)]+2\vec{p}/m\cdot[\frac{1}{2}(\vec{r}+\vec{r}(t'))\frac{j_1(k|\vec{r}+\vec{r}(t')|/2)}{k|\vec{r}+\vec{r}(t')|/2}+$$

$$+\frac{1}{2}(\vec{r}-\vec{r}(t'))\frac{j_1(k|\vec{r}-\vec{r}(t')|/2)}{k|\vec{r}-\vec{r}(t')|/2}-(\vec{r}+\vec{p}t'/m)\frac{j_1(k|\vec{r}+\vec{p}t'/m|)}{k|\vec{r}+\vec{p}t'/m|}+$$

$$+\vec{p}t'/m\frac{j_1(kpt'/m)}{kpt'/m}]$$

Incoherent intermediate scattering function

$$F_k^s(t) = \exp(-k^2t^2/2\beta m)+F_k^{s(2)}(t)$$

$$\varepsilon_k^{s(2)}(t) = F_k^{s(2)}(t)$$

$$F_k^{s(2)}(t) = \frac{1}{2}nk^2\int_o^t dt'\exp(-k^2t'^2/4\beta m)\int d\vec{p}d\vec{r}\varphi(p)g(r)f_k^s(\vec{p}\vec{r};t')$$

$$f_k^s(\vec{p}\vec{r};t') = -(\beta m)^{-1}t'[j_o(k|\vec{r}-\vec{r}(t')|/2)-j_o(kpt'/m)]+2\vec{p}/m\cdot$$

$$[\frac{1}{2}(\vec{r}-\vec{r}(t'))\frac{j_1(k|\vec{r}-\vec{r}(t')|/2)}{k|\vec{r}-\vec{r}(t')|/2}+\vec{p}t'/m\frac{j_1(kpt'/m)}{kpt'/m}]$$

in the second derivative expansion nowhere an approximation is made such as (2.16) in the Ursell expansion and on the other hand not only the second moments but also the fourth moments agree with the corresponding exact moments. A disadvantage of the second derivative expansion is that the expressions (2.56)-(2.59) for the two particle terms are more complex than the two particle expressions (2.31) and (2.32) in the Ursell expansion.

The difference between the straightforward Ursell expansion and the second derivative expansion is a consequence of the different moments on which the expansion of the streaming operator is made: in the Ursell expansion the expansion is directly made, while in the second derivative expansion the expansion is made in the second derivative of $F_k(t)$ and is followed by a double time integration. Of course the exact theory (no restriction to the two particle terms) yields the same results in both theories. The difference between the results of the straightforward Ursell expansion and the results of the second derivative expansion is a measure of the accuracy of this method.

CHAPTER 3

THE URSELL EXPANSION FOR THE HARD SPHERES SYSTEM

In chapter 2 general expressions were derived for the deviations of the intermediate scattering functions and the velocity autocorrelation function as far as the two particle collisions are concerned (see table III). As a first approximation of a real gas of interacting particles we shall in this chapter consider a system of hard spheres. This choice has been motivated by the simpleness of the hard spheres trajectories. On the other hand this assumption is rather drastic and has as a consequence that the theoretical calculations can only be compared with experimental results in a qualitative way. Of course it is possible to compare the hard spheres results with molecular dynamics experiments.

In the first section of this chapter the structure of the hard spheres system will be discussed. In the next section we shall substitute the trajectory of a particle in a hard spheres potential in the general expressions for $\varepsilon_k^{(2)}(t)$, $\varepsilon_k^{s(2)}(t)$ and $C_D^{(2)}(t)$ that were derived in section 2.3. We have already seen that the moments of the two particle terms in the Ursell expansion are not the same as the exact moments. Even the second moment of $F_k(t)$ differs from the exact second moment, due to the approximation that is made in (2.16). Explicit expressions for the moments of the hard spheres Ursell expansion will be given in section 3.3.

In the case of a non singular interaction it is possible to make another expansion, the second derivative expansion (section 2.5), by making use of the antihermiticity of the Liouville operator. In that expansion the first moments do all correspond with the exact moments. Since the hard spheres Liouville operator is not antihermitian, as can be seen from (1.26), such an expansion cannot be made for hard spheres. In section 3.4 another expansion, the Ursell-2 expansion, will be discussed, where also use has been made of the different hermitian properties of the hard spheres Liouville operator. This expansion is only valid for hard spheres. It will be shown that in the Ursell-2 expansion the first moments agree with the exact hard spheres moments. Furthermore it will appear that the deviation $\varepsilon_k^{s(2)}(t)$ of the incoherent intermediate scattering function takes a very simple form: a multiplicative factor times a function only depending on kt. The deviation $C_D^{(2)}(t)$ of the velocity auto-correlation function is in this expansion the same as the exact first moment of $C_D(t)$.

Finally in the last section the results of the hard spheres calculations will be given; they will also be compared with molecular dynamics experiments.

3.1 THE STRUCTURE OF THE HARD SPHERES GAS

The static structure of a fluid or gas will be described by the pair correlation function g(r), which gives the probability to find a particle at a distance r from another particle in the origin. From (1.5) it is clear that, if the interaction potential $\varphi(r)$ is known, one can in principle calculate g(r). However this cannot be done exactly; so some approximation has to be used. It can be done as follows: the Ornstein-Zernike equation (1.10) defines the direct correlation function C(r) in terms of G(r) = g(r)-1. In order to be able to calculate g(r) one must have another relation between C(r) and g(r). For low densities satisfactory results are obtained from the Percus-Yevick equation (Percus, Yevick, 1958):

$$C(r) = (1-\exp(\beta\varphi(r)))g(r) \qquad (3.1)$$

Furthermore hard spheres cannot penetrate into each other so one should require that:

$$g(r) = 0 \quad \text{for} \quad r < \sigma \qquad (3.2)$$

Thiele (1963) and Wertheim (1963, 1964) showed that these equations can be solved exactly for the case of the hard spheres potential. The direct correlation function C(r) appears to be a very simple function because

i) $C(r) = 0$ for $r > \sigma$ as can be seen from (3.1) and

ii) $C(r)$ is a cubic polynomial for $0 < r \leq \sigma$:

$$C(r) = -(1-\eta)^{-4}[(1+2\eta)^2 - 6\eta(1+\eta/2)^2(r/\sigma) + \frac{1}{2}\eta(1+2\eta)^2(r/\sigma)^3] \quad \text{for } 0 < r \leq \sigma \tag{3.3}$$

$$= 0 \quad \text{for } r > \sigma$$

where $\eta = \frac{1}{6}\pi n\sigma^3$. After taking the fourier transform of (3.4) the structure factor S(k) follows immediately from (1.11) as:

$$S(k) = (1-n\sigma^3 f(k\sigma)/(k\sigma))^{-1} \tag{3.4}$$

with

$$f(k\sigma) = -2\pi(1-\eta)^{-4}[-(\eta^3-3\eta+2)\cos k\sigma/k\sigma + 2(5\eta^3-6\eta+1)\sin k\sigma/(k\sigma)^2 + 6\eta(k\sigma)^{-3}\{(7\eta^2+4\eta-2)\cos k\sigma+(2+\eta)^2\} - 24\eta(1+2\eta)^2(k\sigma)^{-4}\{\sin k\sigma+(\cos k\sigma-1)/k\sigma\}] \tag{3.5}$$

The easiest way to obtain the pair correlation function g(r) consists of taking the inverse fourier transform of (3.4) (Mandel et. al., 1970).

It is well known that for intermediate and high densities the Percus-Yevick equation does not give satisfactory results;

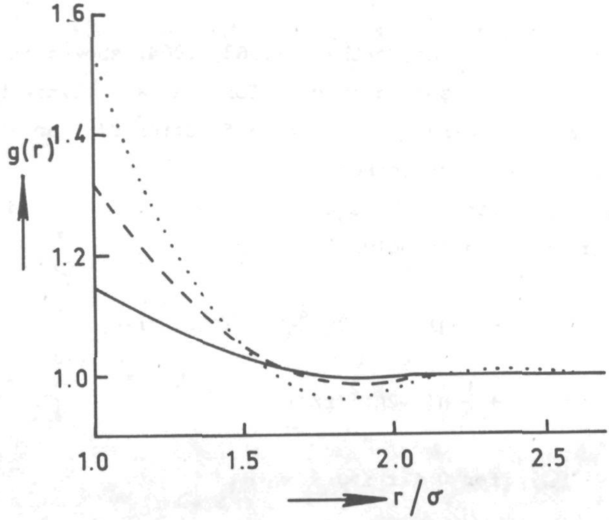


Fig. 2. The hard spheres pair correlation function g(r) for the reduced densities $n\sigma^3 = 0.1$ (full line), $n\sigma^3 = 0.2$ (dashed line) and $n\sigma^3 = 0.3$ (dotted line).

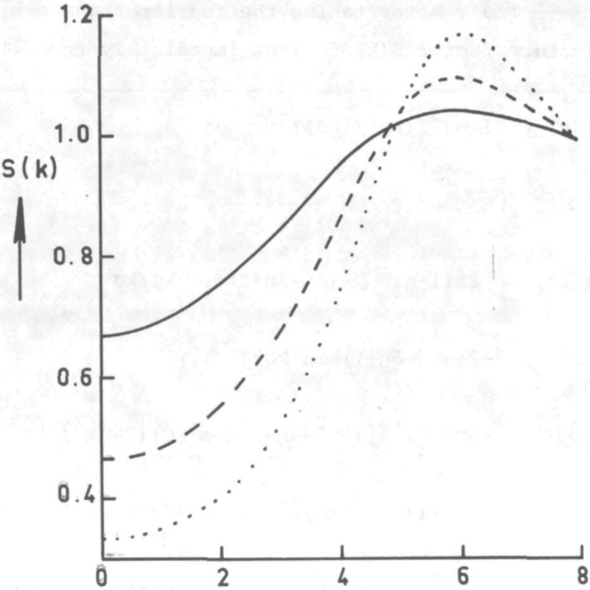


Fig. 3. The hard spheres structure factor S(k). The densities are the same as in fig. 2.

for that case Verlet and Weis (1972) have improved the exact solution of the Percus-Yevick equation. This regime falls however outside the domain where we can handle the time dependence of the correlation functions by an expansion as discussed in chapter 2.

Both g(r) and S(k) are calculated for the reduced densities $n\sigma^3 = 0.1$, 0.2 and 0.3 (see fig. 2 and 3).

3.2 THE URSELL EXPANSION FOR THE HARD SPHERES SYSTEM

We shall now in this section apply to the hard spheres system the general expressions for the deviations $\varepsilon_k^{(2)}(t)$, $\varepsilon_k^{s(2)}(t)$ and $C_D^{(2)}(t)$ which were obtained in chapter 2 (see table III). Therefore we have to substitute the hard spheres position $\vec{r}(t)$ and momentum $\vec{p}(t)$ in these expressions.

The trajectory can be found as follows (see fig. 4): suppose that one particle is fixed in the origin O of the coordinate

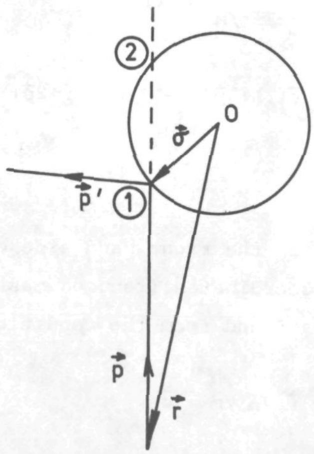


Fig. 4. The hard spheres collision. The initial position and momentum is $\vec{r}$ resp. $\vec{p}$; the post-collisional momentum is $\vec{p}\,'$. The collision takes place at $\vec{\sigma}$.

system and that the other particle has at time $t = 0$ an initial position $\vec{r}$ and an initial momentum $\vec{p}$. The latter particle collides at time $t = \tau$ and position $\vec{r} = \vec{\sigma}$ with the fixed sphere. Since we are considering hard spheres the collision is elastic and instantaneous. The post-collisional momentum $\vec{p}'$ is easily calculated from the conservation laws of energy and momentum as

$$\vec{p}' = \vec{p}-2(\vec{p}\cdot\hat{\sigma})\hat{\sigma} \tag{3.6}$$

where $\hat{\sigma}$ is a unit vector in the direction of $\vec{\sigma}$. The momentum $\vec{p}(t)$ as a function of time becomes:

$$\vec{p}(t) = \vec{p}-2(\vec{p}\cdot\hat{\sigma})\hat{\sigma}\ \theta(t-\tau) \tag{3.7}$$

where $\theta(t-\tau)$ is the unit step function defined in (1.23). The trajectory $\vec{r}(t)$ can now immediately be written as:

$$\begin{aligned} \vec{r}(t) &= \vec{r}+2\vec{p}t/m && \text{for } 0 < t \leq \tau \\ &= \vec{r}(\tau)+2\vec{p}'(t-\tau)/m = \vec{r}+2\vec{p}\tau/m+2\vec{p}'(t-\tau)/m && \\ & && \text{for } t > \tau \end{aligned} \tag{3.8}$$

The factor 2 in the right hand side of (3.8) reflects the use of relative coordinates (reduced mass = m/2). The collision time τ can be found from the condition:

$$\vec{r}(\tau) = \vec{r}+2\vec{p}\tau/m = \vec{\sigma}$$

As $|\vec{\sigma}| = \sigma$ is fixed, τ follows from:

$$r^2+4\vec{r}\cdot\vec{p}\tau/m+4p^2\tau^2/m^2 = \sigma^2 \tag{3.9}$$

This quadratic equation has two solutions for τ of which we have to take the smallest one corresponding to the point 1 in fig. 4. The other solution (point 2 in fig. 4) gives the second intersection of the trajectory with the sphere in the case that the particle would stream freely through the sphere.

The above found expressions for $\vec{p}(t)$ and $\vec{r}(t)$ can now be inserted in the expressions for the deviations (2.31), (2.32) and (2.34). This calculation will not be done in detail here but will be carried out in appendix E.

It appears, as can easily be seen from dimensional analysis, that $\varepsilon_k^{(2)}(t)$ and $\varepsilon_k^{s(2)}(t)$ depend only on the following three quantities:

i) a reduced wave vector $k^* = k\sigma$

ii) a reduced density $n^* = n\sigma^3$

and iii) a dimensionless time $t^* = t/\sigma(\beta m)^{1/2}$.

The deviation of the velocity autocorrelation function $C_D^{(2)}(t)$ depends only on n^* and t^*.

3.3 THE MOMENTS OF THE TWO PARTICLE TERMS OF THE HARD SPHERES URSELL EXPANSION

The moments of the hard spheres Ursell expansion in the two particle approximation are derived in completely the same way as the moments in the case of a non singular interaction (section 2.4). Because the calculation is rather complicated it is carried out in detail in appendix F. The results for the coherent intermediate scattering function are:

$$M_o^u(k) = S(k)$$

$$M_1^u(k) = 0$$

$$M_2^u(k) = -S(k)(4\pi nk\sigma^2 g(\sigma) j_1(k\sigma)/\beta m + k^2/\beta m) \qquad (3.10)$$

$$M_3^u(k) = 8\pi^{1/2} nS(k)(\beta m)^{-3/2}[-2k\sigma^2 g'(\sigma) j_1(k\sigma) + g(\sigma)\{(k\sigma)^2/3 - k\sigma \sin k\sigma - 2\cos k\sigma + 2\sin k\sigma/k\sigma\}]$$

where $j_1(k\sigma)$ is the first order spherical bessel function (2.36) and $g'(\sigma)$ the first derivative of the pair correlation function at $r = \sigma_+$.

Comparing (3.10) with (1.45) we see that the first Ursell moments differ considerably from the corresponding exact moments. This discrepancy is due to the approximation (2.16) for the m-particle static correlation function. In fig. 5 the

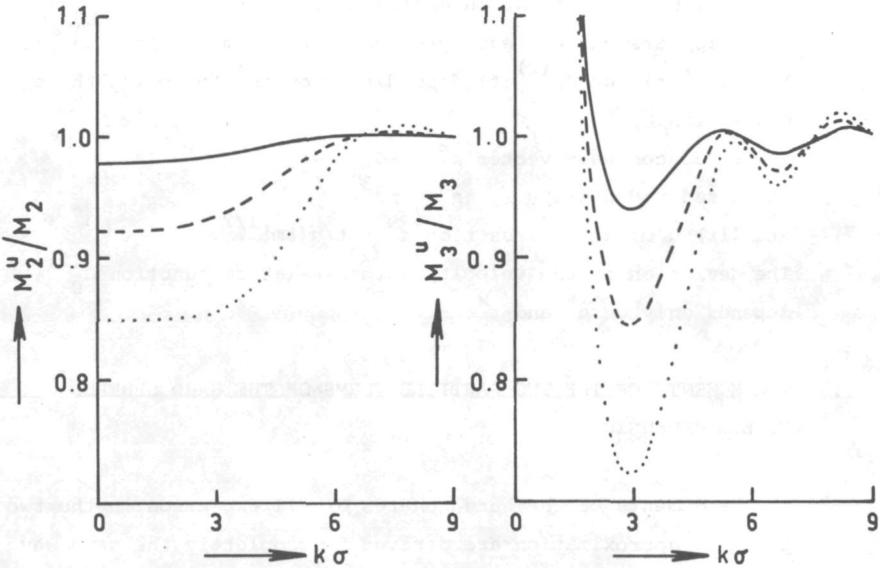


Fig. 5. The ratio M_2^u/M_2 of the Ursell second moment and the exact second moment (left) and the ratio M_3^u/M_3 of the Ursell and the exact third moment (right).

ratios of the Ursell and exact second and third moment are shown.

The expression for $M_2^u(k)$ can be written in another form by noting that for very low densities, where $g(r) = \theta(r-\sigma)$, the structure factor $S^o(k)$ follows from (1.9) as:

$$S^o(k) = 1-4\pi n\sigma^2 j_1(k\sigma)/k$$

so that the expression for $M_2^u(k)$ becomes:

$$M_2^u(k) = S(k)[k^2 g(\sigma)\{S^o(k)-1\}/\beta m - k^2/\beta m]$$

Because in this low density limit $S^o(k) \simeq 1$ one sees that $M_2^u(k)$ approaches its exact value.

The first moments of the incoherent intermediate scattering function $F_k^s(t)$ and of the velocity autocorrelation function $C_D(t)$ agree completely with the exact moments (1.46) and (1.47).

3.4 THE URSELL-2 EXPANSION FOR HARD SPHERES

It appeared in the last section that the first moments of the two particle term of the Ursell expansion of the intermediate scattering function $F_k(t)$ for hard spheres do not agree with the exact moments. The reason is the same as in the case of a continuous potential (section 2.4): the splitting of $F_k(t)$ in two parts $F_k^A(t)$ and $F_k^B(t)$ whereafter $F_k^B(t)$ is again connected to $F_k^A(t)$ by means of the approximation (2.16) for the static (m+1)-particle distribution function. To avoid this splitting the second derivative expansion was introduced where the A- and B-terms were absent and that yielded the correct moments. Because, as from (1.26) can be seen, the hard spheres Liouville operator L_+ is not antihermitian the second derivative expansion is not applicable for hard spheres.

An alternative for hard spheres can be found by making use of the binary collision expansion (Ernst et. al., 1969) of the streaming operator:

$$\begin{aligned} \exp(tL) &= \exp(tL_o)+\exp(tL_o)\star\sum_\alpha T_+(\alpha)\exp(tL) \\ &= \exp(tL_o)+\exp(tL)\star\sum_\alpha T_+(\alpha)\exp(tL_o) \end{aligned} \tag{3.11}$$

with the convolution integral defined by:

$$f(t)\star g(t) = \int_{o}^{t} dt_1 f(t-t_1)g(t_1) \tag{3.12}$$

Expression (3.11) may be verified by differentiating with respect to the time t. The summation runs over all pairs of particles α and $T_+(\alpha)$ is the interaction part of the hard spheres Liouville operator (1.22) as far as the pair α is concerned.

The expansion can be obtained by substituting for exp(tL) again the whole expression (3.11), resulting in:

$$\begin{aligned} \exp(tL) = {} & \exp(tL_o)+\exp(tL_o)\star\sum_{\alpha} T_+(\alpha)\exp(tL_o) \\ & +\exp(tL_o)\star\sum_{\alpha} T_+(\alpha)\exp(tL_o)\star\sum_{\beta} T_+(\beta)\exp(tL_o)+\ldots \end{aligned} \tag{3.13}$$

This procedure may be continued till the desired number of binary collisions is reached.

We will now consider some time dependent correlation function $\langle f(0)g(t)\rangle$ where f and g are arbitrary time dependent functions of the phase space variables. With (1.12), (1.13) and (3.13) we write this correlation function in the following form:

$$\begin{aligned} \langle f(0)g(t)\rangle &= \langle f(0)\exp(tL)g(0)\rangle \\ &= \langle f(0)\exp(tL_o)g(0)\rangle \\ &\quad + \langle f(0)\exp(tL_o)\star\sum_{\alpha} T_+(\alpha)\exp(tL_o)g(0)\rangle \\ &\quad + \langle f(0)\exp(tL_o)\star\sum_{\alpha} T_+(\alpha)\exp(tL_o)\star\sum_{\beta} T_+(\beta) \\ &\qquad \exp(tL_o)g(0)\rangle \\ &\quad + \text{ terms containing three and more collisions.} \end{aligned} \tag{3.14}$$

All operators in (3.14) work on the functions following the operators. One observes that this expansion is similar to the Ursell expansion derived in chapter 2. The first term gives the free streaming, the second term contains the two particle collisions and the next terms are concerned with higher order collisions.

Just as in the case of the second derivative expansion for continuous interactions a more symmetric expression is obtained by shifting one Liouville operator to the left in the second term of (3.14), leading to:

$$\langle [\exp(tL_o^{\dagger})f(0)] \star \sum_{\alpha} T_{+}(\alpha)\exp(tL_o)g(0)\rangle$$

where $L_o^{\dagger}$ is the hermitian conjugate of L_o, defined in (1.17). From (A.9) one obtains the following explicit expression for $L_o^{\dagger}$:

$$L_o^{\dagger} = -L_o - \sum_{\alpha} K(\alpha)$$

with (3.15)

$$K(\alpha) = \delta(r_{\alpha}-\sigma)\hat{r}_{\alpha}\cdot\vec{p}_{\alpha}/m$$

where $\vec{p}_{\alpha}$ and $\vec{r}_{\alpha}$ are the relative momentum and position of the particles of pair α. One verifies easily by differentiation with respect to t that for $\exp(tL_o^{\dagger})$ an expression holds analogous to (3.11) for the full streaming operator exp(tL):

$$\exp(tL_o^{\dagger}) = \exp(-tL_o) - \exp(tL_o^{\dagger}) \star \sum_{\alpha} K(\alpha)\exp(-tL_o) \qquad (3.16)$$

where use has been made of (3.15). Substitution of (3.16) in the second term of (3.14) results in the following expression for the correlation function:

$$\langle f(0)g(t)\rangle = \langle f(0)\exp(tL_o)g(0)\rangle$$

$$+\langle[\exp(-tL_o)f(0)]\star\sum_{\alpha}T_+(\alpha)\exp(tL_o)g(0)\rangle$$

$$-\langle[\exp(tL_o^{\dagger})\star\sum_{\beta}K(\beta)\exp(-tL_o)f(0)]\star\sum_{\alpha}T_+(\alpha)\exp(tL_o)g(0)\rangle$$

$$+\langle f(0)\exp(tL_o)\star\sum_{\alpha}T_+(\alpha)\exp(tL_o)\star\sum_{\beta}T_+(\beta)\exp(tL_o)g(0)\rangle$$

$$+ \;\ldots. \qquad (3.17)$$

We shall now show that the third term of (3.17) is needed to obtain a symmetric version of the two collisions term (the fourth term). To do this we shift in the third term $\exp(tL_o^{\dagger})$ again to the right and in the fourth term $\exp(tL_o)\sum_{\alpha}T_+(\alpha)$ to the left; after addition of both terms the result is:

$$\langle[-\sum_{\alpha}K(\alpha)\exp(-tL_o)f(0)+\sum_{\alpha}T_+^{\dagger}(\alpha)\exp(tL_o^{\dagger})f(0)]$$

$$\star\exp(tL_o)\star\sum_{\beta}T_+(\beta)\exp(tL_o)g(0)\rangle$$

In appendix A (A.16) we have derived for the hermitian conjugate $T_+^{\dagger}(\alpha)$ *of the interaction part of the hard spheres* Liouville operator the expression:

$$T_+^{\dagger}(\alpha) = T_-(\alpha)+K(\alpha) \qquad (3.18)$$

with $K(\alpha)$ given in (3.15). Substitution of (3.16) and (3.18) in the expression above, thereby restricting ourselves to the free streaming part $\exp(-tL_o)$ of (3.16), leads to the following expression for the correlation function:

$$<f(0)g(t)> = <f(0)\exp(tL_o)g(0)>$$

$$+<[\exp(-tL_o)f(0)]^{\star}\sum_{\alpha} T_+(\alpha)\exp(tL_o)g(0)>$$

$$+<[\sum_{\alpha} T_-(\alpha)\exp(-tL_o)f(0)]^{\star}\exp(tL_o)^{\star}\sum_{\beta} T_+(\beta)\exp(tL_o)g(0)>$$

$$+ \;.... \qquad (3.19)$$

The second term on the right hand side of (3.16) is again needed to symmetrize the three collisions term etc. One sees again that the first and second term of (3.19) contain the free streaming and the two particle collisions, while in the other terms two and more collisions are involved. The expansion (3.19) will in the following be referred to as the Ursell-2 expansion. In the remaining of this section the Ursell-2 expansion of the intermediate scattering functions and of the velocity autocorrelation function will be discussed as far as the two particle terms are concerned.

a) The incoherent intermediate scattering function

From (1.28), (3.12) and (3.19) it is seen that the self function $F_k^s(t)$ consists in the two particle approximation of two parts:

$$F_k^s(t) = F_k^{s(1)}(t) + F_k^{s(2)}(t) \qquad (3.20)$$

with the free streaming part given by:

$$F_k^{s(1)}(t) = N^{-1}\sum_{i=1}^{N} <\exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL_o)\exp(i\vec{k}\cdot\vec{r}_i)> \qquad (3.21)$$

while the two particle collisions yield:

$$F_k^{s(2)}(t) = N^{-1}\sum_{\alpha}\int_o^t dt_1 \sum_{i=1}^{N} <[\exp(-(t-t_1)L_o)\exp(-i\vec{k}\cdot\vec{r}_i)] \\ T_+(\alpha)\exp(t_1L_o)\exp(i\vec{k}\cdot\vec{r}_i)> \qquad (3.22)$$

The free streaming part $F_k^{s(1)}(t)$ is the same as in the Ursell expansion and follows from (2.21) as:

$$F_k^{s(1)}(t) = \exp(-k^2t^2/2\beta m) \qquad (3.23)$$

The calculation of $F_k^{s(2)}(t)$ is rather complicated and will be discussed in appendix G; the result is:

$$F_k^{s(2)}(t) = \pi^{1/2}n\sigma^3 g(\sigma)(k\sigma)^{-1}f(\lambda) \qquad (3.24)$$

with

$$f(\lambda) = \lambda^{-1}\exp(-\lambda^2/4)\int_0^\infty du\, u\, \exp(-u^2/4)[\, 2\sin(\lambda u/2)\mathrm{Si}(\lambda u) + 2\cos(\lambda u/2)\{\mathrm{Ci}(\lambda u)-\ln(\lambda u)-\gamma\}-\lambda u\,\sin(\lambda u/2)] \qquad (3.25)$$

where λ is a dimensionless variable, defined by:

$$\lambda = (\beta m)^{-1/2}kt, \qquad (3.26)$$

$\gamma = 0.577216$ is the Euler constant and Si and Ci are the sine- and cosine-integrals (Abramowitz, Stegun, 1965).

One sees that $F_k^{s(2)}(t)$ takes a very simple form: a multiplicative factor only depending on the reduced density $n\sigma^3$ and the reduced wavevector $k\sigma$ times a function $f(\lambda)$ only depending on $(\beta m)^{-1/2}kt$. Fig. 6 shows the function $f(\lambda)$ explicitly.

b) The coherent intermediate scattering function

The coherent function $F_k(t)$ can be written analogous to the self function and with the aid of (1.28), (3.12) and (3.19), as the sum of two terms:

$$F_k(t) = F_k^{(1)}(t)+F_k^{(2)}(t) \qquad (3.27)$$

with the free streaming and the two particle terms given by:

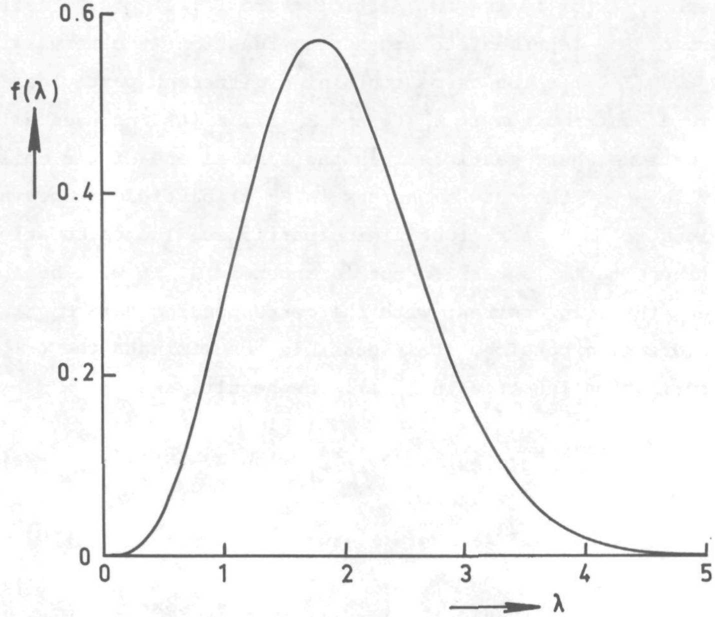


Fig. 6. The function $f(\lambda)$ ($\lambda = (\beta m)^{-1/2}kt$), which is discussed in the text.

$$F_k^{(1)}(t) = N^{-1}\langle \sum_{i=1}^{N} \exp(-i\vec{k}\cdot\vec{r}_i)\exp(tL_o) \sum_{j=1}^{N} \exp(i\vec{k}\cdot\vec{r}_j)\rangle$$

$$F_k^{(2)}(t) = N^{-1}\sum_{\alpha}\int_o^t dt_1 \langle [\exp(-(t-t_1)L_o) \sum_{i=1}^{N} \exp(-i\vec{k}\cdot\vec{r}_i)] \quad (3.28)$$

$$T_+(\alpha)\exp(t_1L_o) \sum_{j=1}^{N} \exp(i\vec{k}\cdot\vec{r}_j)\rangle$$

The free streaming term $F_k^{(1)}(t)$ yields again the same result (2.20) as in the Ursell expansion:

$$F_k^{(1)}(t) = S(k)\exp(-k^2t^2/2\beta m) \quad (3.29)$$

We write the two particle term as the sum of three terms:

$$F_k^{(2)}(t) = F_k^{s(2)}(t)+F_k^A(t)+F_k^B(t) \quad (3.30)$$

where $F_k^{s(2)}(t)$ is the two particle term (3.24) of the self part of the intermediate scattering function (the terms with i=j in (3.28)). The terms containing different particles (i≠j) give a contribution to $F_k^A(t)$ and $F_k^B(t)$. $F_k^A(t)$ includes all situations where particle i is the same as one of the colliding particles of the pair α whereas in $F_k^B(t)$ particle i does not belong to this pair of colliding particles. The calculation of these terms is carried out in appendix G. It will be shown there that, in contrast with the corresponding term $F_k^B(t)$ in the Ursell expansion, it is possible to eliminate the triple distribution function in $F_k^B(t)$. The results are:

$$F_k^A(t) = \pi^{1/2} n^* g(\sigma) \exp(-\lambda^2/4) t^* \int_{-1}^{1} d\tau \int_{o}^{1} du \exp(-\lambda^2\tau^2(1-u^2)/4)$$
$$\int_{o}^{\infty} dw\ w \exp(-w^2/4)[\cos(u(k^*+\lambda w/2)) - \cos(u(k^*+\lambda w\tau/2))]$$
$$F_k^B(t) = \frac{1}{2} \pi^{1/2} \lambda \exp(-\lambda^2/4) \operatorname{erf}(\lambda/2)[4\pi n^* j_1(k^*) g(\sigma)/k^* + S(k^*) - 1] \tag{3.31}$$

where the dimensionless variables n^*, k^* and t^* were introduced at the end of section 3.2, $\lambda = k^* t^*$ and $\operatorname{erf}(\lambda/2)$ is the error function (Abramowitz, Stegun, 1965). One sees that in contradiction to the Ursell expansion, where an approximation for the static (m+1)-particle correlation function was needed to express $F_k^B(t)$ in terms of $F_k^A(t)$ (see section 2.2), in the Ursell-2 expansion this term can be calculated exactly and takes finally a simple form.

c) The velocity autocorrelation function

From (1.34), (3.12) and (3.19) one observes that the velocity autocorrelation function can be written in the two particle approximation as:

$$C_D(t) = \frac{1}{3}\beta m\langle\vec{v}_1(0)\cdot\vec{v}_1(t)\rangle$$

$$= \frac{1}{3}\beta m\langle\vec{v}_1\cdot\exp(tL_o)\vec{v}_1\rangle \qquad (3.32)$$

$$+ \frac{1}{3}\beta m\sum_\alpha\int_o^t dt_1\langle[\exp(-(t-t_1)L_o)\vec{v}_1]\cdot T_+(\alpha)\exp(t_1L_o)\vec{v}_1\rangle$$

Because the free streaming operator L_o leaves the velocity $\vec{v}_1$ unchanged this reduces to:

$$C_D(t) = \frac{1}{3}\beta m\langle\vec{v}_1\cdot\vec{v}_1\rangle + \frac{1}{3}\beta m\sum_\alpha\int_o^t dt_1\langle\vec{v}_1\cdot T_+(\alpha)\vec{v}_1\rangle \qquad (3.33)$$

It is clear that the free streaming term yields the ideal gas value 1. For the two particle interaction term the first moment (1.47) of $C_D(t)$ is obtained. Thus:

$$C_D(t) = 1-\frac{8}{3}\pi^{1/2}g(\sigma)n^*t^* \qquad (3.34)$$

The moments of the correlation functions in the Ursell-2 expansion are calculated in the same way as in the Ursell expansion. The computation is carried out in appendix H and leads to the result that, in contrast with the Ursell expansion for hard spheres, the first moments all agree with the exact hard spheres moments (1.45), (1.46) and (1.47). Another advantage of the Ursell-2 expansion is that the expressions for the correlation functions are much easier. For the incoherent intermediate scattering function (3.24) and the velocity autocorrelation function (3.34) this is quite obvious and for the coherent intermediate scattering function (3.31) one sees immediately that the pair correlation function g(r) does not occur in the integrand, so that the integral is independent of the density; g(r) is only present as a multiplicative factor $g(\sigma)$ and in $F_k^B(t)$ as the structure factor S(k). Also compared with the second derivative expansion for non singular

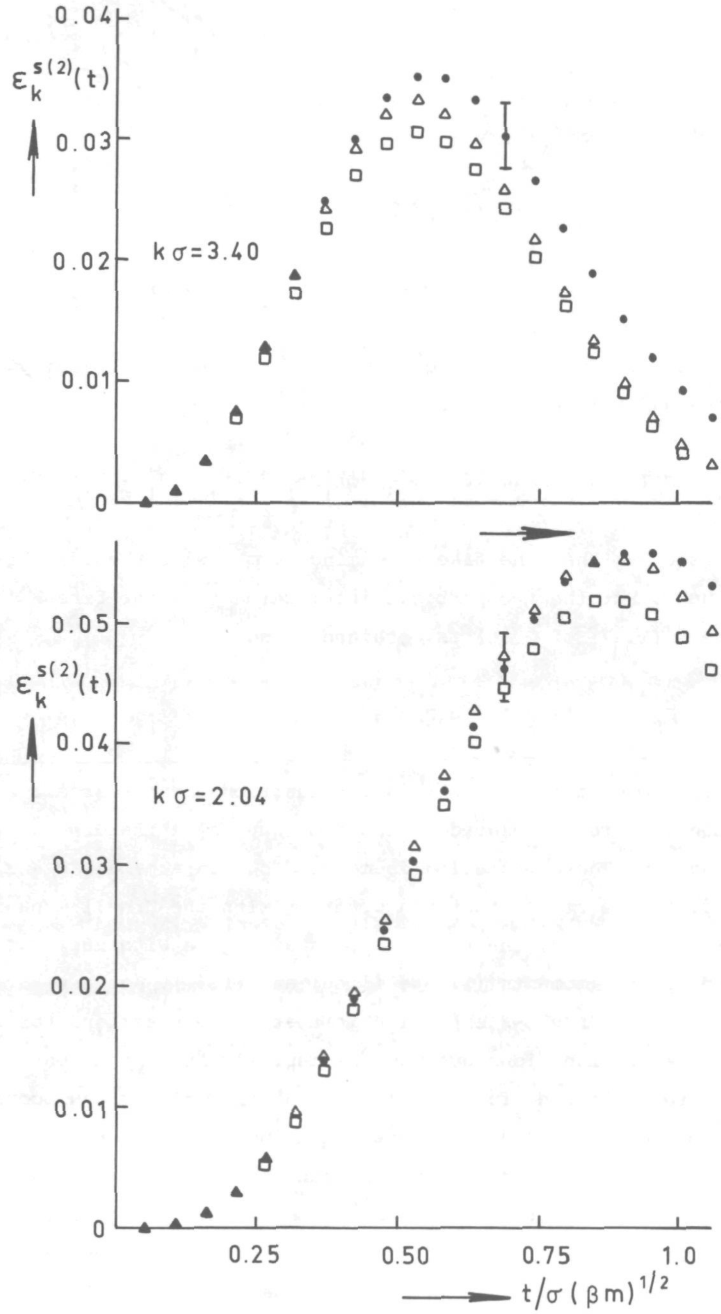


Fig. 7. The incoherent deviation $\varepsilon_k^s(t)$ of a hard spheres system with density $n\sigma^3=0.098$, as calculated with the Ursell expansion (squares), the Ursell-2 expansion (triangles) and with molecular dynamics (circles).

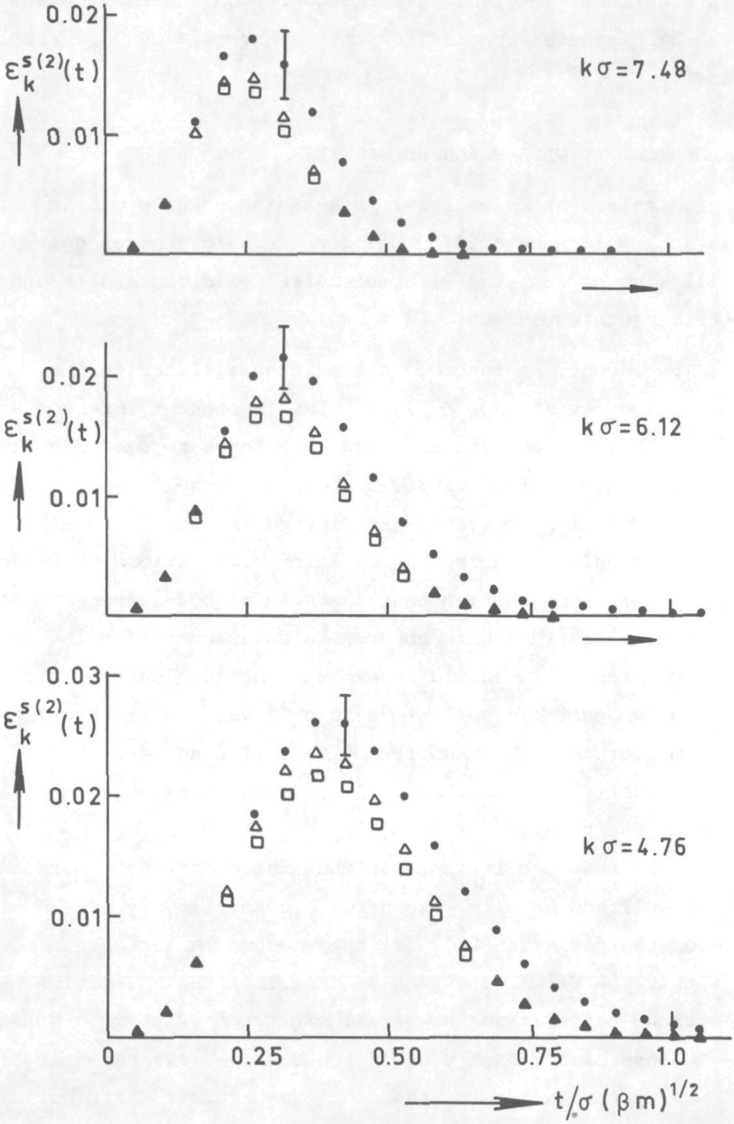


Fig. 7. The incoherent deviation $\varepsilon_k^s(t)$ of a hard spheres system with density $n\sigma^3=0.098$, as calculated with the Ursell expansion (squares), the Ursell-2 expansion (triangles) and with molecular dynamics (circles).

interactions (see table IV) the corresponding expressions in the hard spheres Ursell-2 expansion have a much more simple form.

3.5 NUMERICAL RESULTS FOR HARD SPHERES

In this section we shall present the results of the calculations which are carried out for the hard spheres system. They will also be compared with molecular dynamics results and with the moments expansion.

a) The incoherent intermediate scattering function.

The deviation $\varepsilon_k^{s(2)}(t)$ of the incoherent intermediate scattering function is calculated for a reduced density $n\sigma^3 = 0.098$. The results of both the Ursell expansion and the Ursell-2 expansion are plotted in fig. 7, together with the results of molecular dynamics calculations of Lyklema (1975). One observes that there is a good agreement between the theoretical hard spheres calculations and molecular dynamics. This should be expected because our restriction to two particle collisions is only valid when the time t is smaller than the mean free time τ (for $n\sigma^3 = 0.098$ is $\tau/\sigma(\beta m)^{1/2} = (\sqrt{2}\pi n\sigma^3)^{-1} = 2.3$, which is twice as much as our largest time).

Furthermore it is clear that the differences between the Ursell and Ursell-2 expansion are small; only at the maximum of the deviation $\varepsilon_k^{s(2)}(t)$ they become larger. It is obvious that the Ursell-2 expansion describes the short time behaviour better than the Ursell expansion which is a consequence of the fact that in the Ursell-2 expansion nowhere an approximation for the static m-particle distribution function is made such as (2.16) in the Ursell expansion.

In fig. 8 the theoretical results are compared with the hard spheres moments expansion. One sees that the moments expansion is only valid for very short times (up to $t/\sigma(\beta m)^{1/2} \simeq 0.1$).

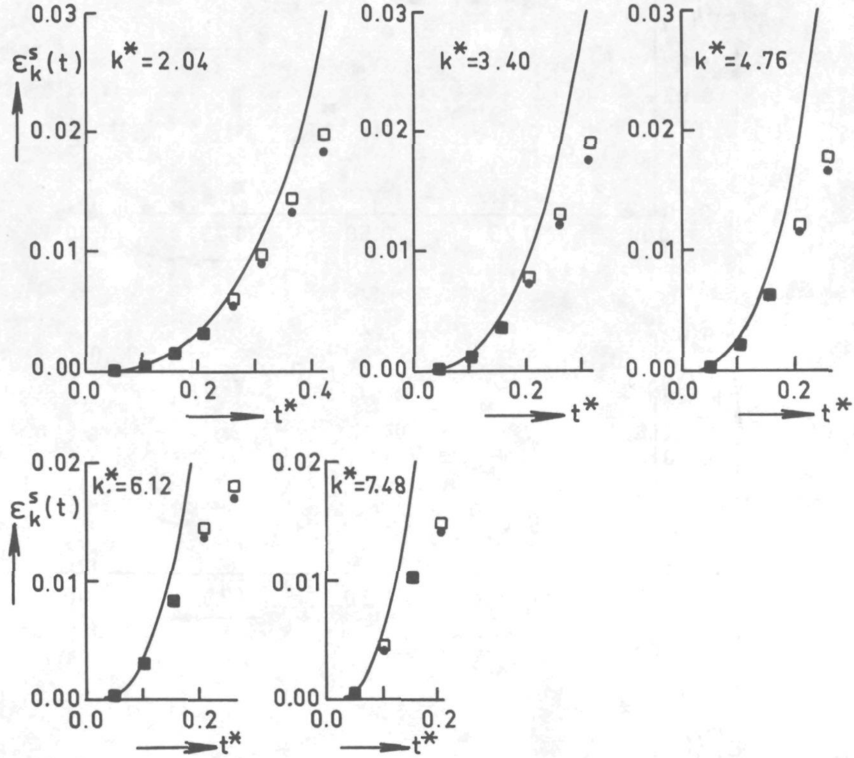


Fig. 8. The incoherent deviation $\varepsilon_k^s(t)$ of a hard spheres system with density $n\sigma^3 = 0.098$ as calculated with the Ursell expansion (circles) and the Ursell-2 expansion (squares), compared with the hard spheres moments expansion (full line) ($k^* = k\sigma$ and $t^* = t/\sigma(\beta m)^{1/2}$).

b) *The coherent intermediate scattering function.*

In fig. 9 the numerical results of the calculations on the deviation $\varepsilon_k^{(2)}(t)$ of the coherent intermediate scattering function are shown for a density $n\sigma^3 = 0.098$. The differences between the deviations of the Ursell- and the Ursell-2 expansion are also small for the coherent function. Fig. 10 shows the theoretical results compared with the moments expansion; one observes that, just as for the incoherent deviations, the validity of the moments expansion is

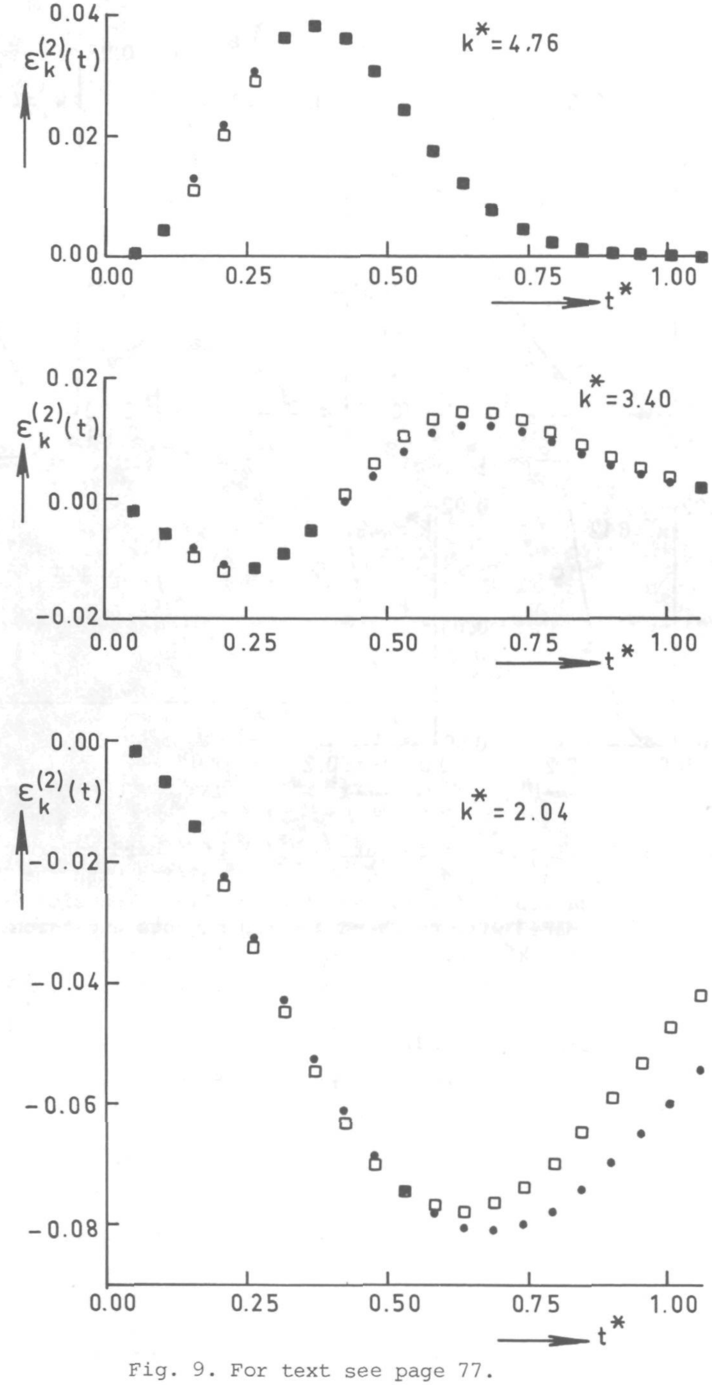


Fig. 9. For text see page 77.

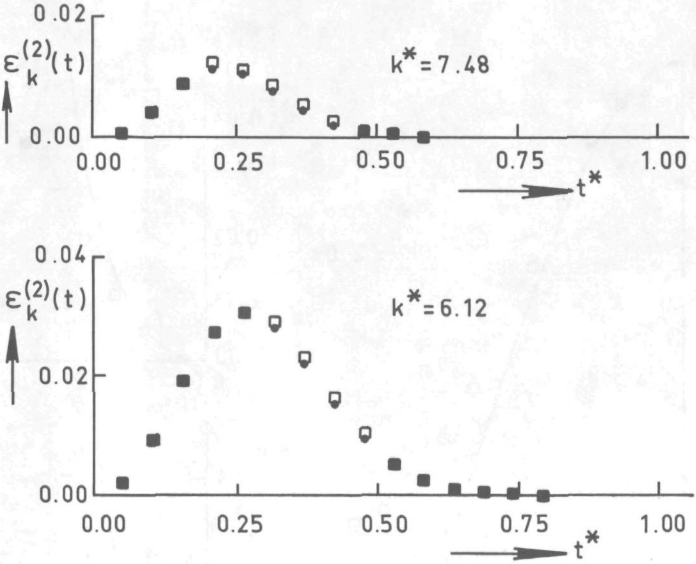


Fig. 9. The hard spheres coherent deviation $\varepsilon_k^{(2)}(t)$ for a density $n\sigma^3$=0.098. The circles denote the values obtained by the Ursell expansion; the squares give the values of the Ursell-2 expansion ($k^* = k\sigma$, $t^* = t/\sigma(\beta m)^{1/2}$).

restricted to very short times (up to $t/\sigma(\beta m)^{1/2} \approx 0.1$).

c) The velocity autocorrelation function.

In fig. 11 the results of the calculations on the Ursell- and the Ursell-2 expansion of the velocity autocorrelation function are plotted, together with the molecular dynamics calculations of Lyklema (1975). One should keep in mind that the Ursell-2 expansion is the same as the moments expansion up to the first moment (see (3.34)). We notice that also the theoretical calculated velocity autocorrelation functions follow the molecular dynamics results quite well.

The validity of the hard spheres moments expansion is, in contrast with the moments expansion for continuous potentials, not restricted by the duration of the collision. This is clearly demonstrated by fig. 11, where one sees that the moments ex-

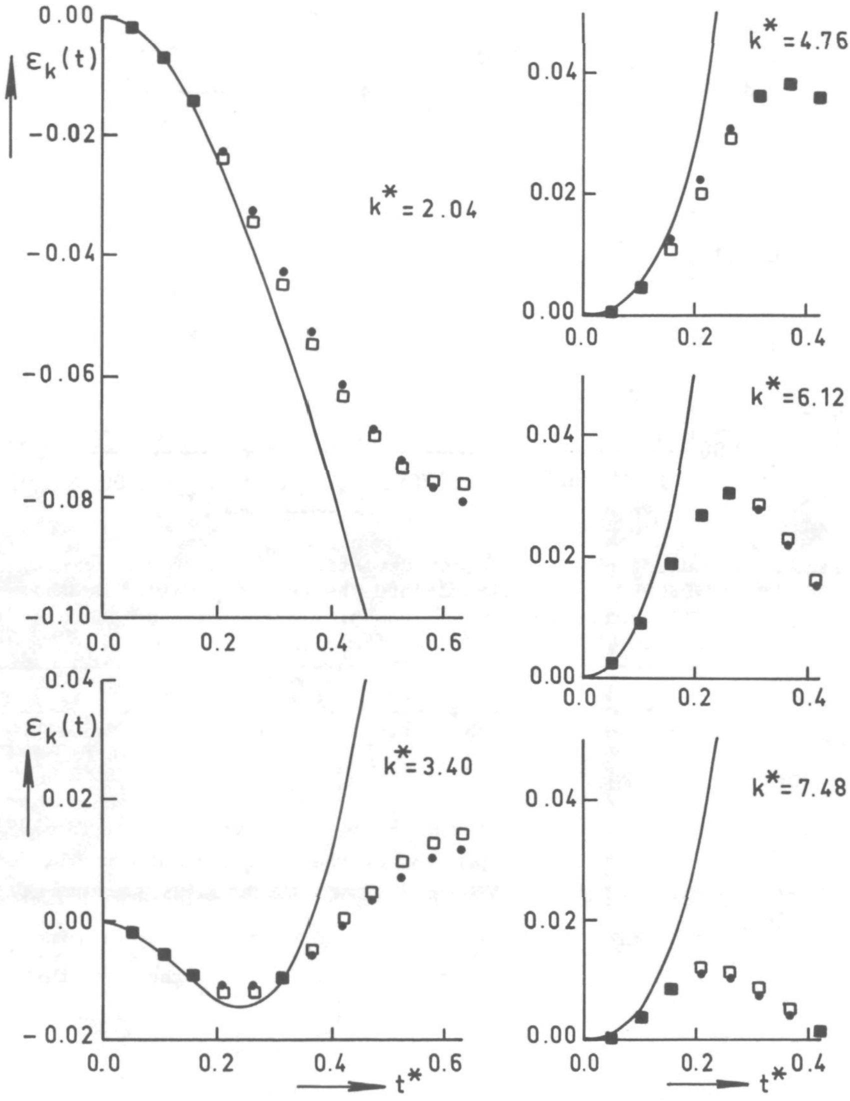


Fig. 10. The hard spheres coherent deviation $\varepsilon_k(t)$ for a density $n\sigma^3=0.098$ as calculated with the Ursell expansion (circles) and the Ursell-2 expansion (squares), compared with the hard spheres moments expansion (full line) ($k^*=k\sigma$, $t^*=t/\sigma(\beta m)^{1/2}$).

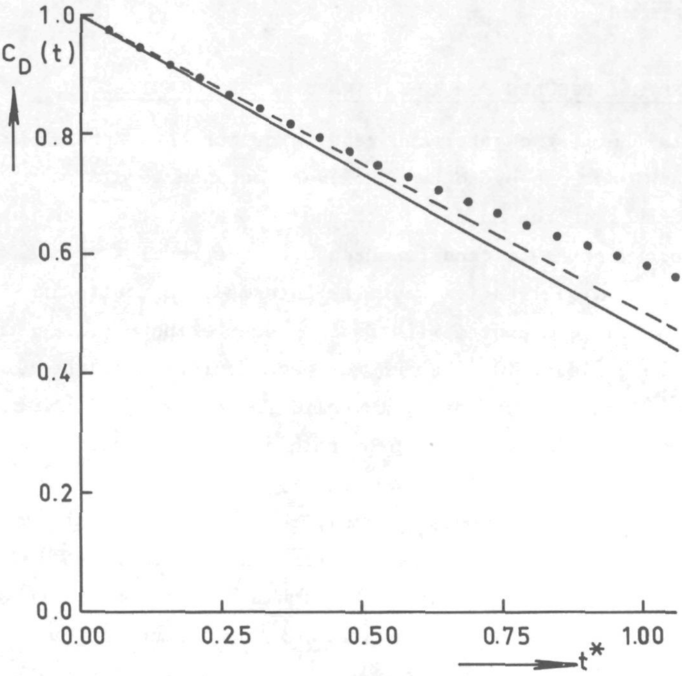


Fig. 11. The hard spheres velocity autocorrelation function $C_D(t)$ for a density $n\sigma^3=0.098$ ($t^*=t/\sigma(\beta m)^{1/2}$) as obtained by the Ursell expansion (dashed line) and the Ursell-2 expansion (full line; identical with the hard spheres moments expansion). The circles denote the molecular dynamics results (Lyklema).

pansion (in this case identical with the Ursell-2 expansion) follows the Ursell expansion quite well. For the intermediate scattering functions the convergence becomes poorer as k grows larger. This is due to the fact that the third moments (1.45) and (1.46) are *proportional* to k^2 so that the terms with t^3 become relatively larger as k becomes larger and have to be compensated by the fourth and higher moments, which are not yet known.

CHAPTER 4

NUMERICAL RESULTS FOR THE LENNARD-JONES POTENTIAL

In the last chapter the results of the hard spheres Ursell expansions were presented. However, because we did only take into account the hard core of the interaction, we can only expect that these results agree with the results of measurements in a qualitative way. The intermediate scattering functions can be measured with neutron scattering experiments on a time scale of 10^{-12} s and for wave vectors k of the order of 1 $\AA^{-1}$. Because our theory is valid for times up to the mean free time, which is inversely proportional to the density, we are primarily interested in low density neutron scattering experiments. Such experiments can only be done for systems with a large scattering cross section like Ar^{36} (Andriesse, 1970). Therefore we have carried out calculations for a system with a Lennard-Jones (12,6) potential, which accounts very well for the equilibrium properties of noble gases like argon (Verlet, 1967, 1968).

In the case of the Lennard-Jones potential, defined by:

$$\varphi(r) = 4\varepsilon((\sigma/r)^{12}-(\sigma/r)^{6}) \qquad (4.1)$$

where ε is the depth of the potential and σ the molecular diameter, the calculations are much more complicated than in the case of hard spheres, because it is not possible to give an analytical expression for the trajectories such as (3.8) for hard spheres. The equation for the trajectory can be solved by integration for a spherical potential such as (4.1), but such an integration procedure is more laborious than straightforward integration of the equations of motion. We have solved the equations of motion numerically by using the prescription of Verlet (1967).

The integrals that occur in the expressions for the deviations of the intermediate scattering functions and of the velocity autocorrelation function (see tables III and IV) are calculated by means of Monte Carlo integration (Hammersley, Handscomb, 1967), which we shall here describe briefly. Suppose we have the following multidimensional integral:

$$F = \int f(\vec{x})\, d\vec{x} \qquad (4.2)$$

over the n-dimensional hypercube, $f(\vec{x})$ being a given function. The simplest Monte Carlo procedure (crude Monte Carlo) consists of selecting a sequence of M independent, uniformly distributed points $\vec{x}_i$, i = 1,2,..,M in the hypercube and calculating the average value:

$$F_M = M^{-1} \sum_{i=1}^{M} f(\vec{x}_i) \qquad (4.3)$$

over this M points. It is possible to show that the expectation value of this estimate is equal to the desired integral:

$$\langle F_M \rangle = F \qquad (4.4)$$

while the square of its standard deviation σ follows from:

$$\sigma^2 = M^{-1} \int d\vec{x} (f(\vec{x}) - F)^2 \qquad (4.5)$$

Thus by increasing the number of points M the expected error can be made as small as desired. Assuming that $f(\vec{x})$ is roughly proportional to a known positive function $g(\vec{x})$, so that the regions which make important contributions to the integral of $f(\vec{x})$ are also important regions for the integral

$$G = \int g(\vec{x})\, d\vec{x} \qquad (4.6)$$

we can write:

$$F = G \int d\vec{x}\ h(\vec{x})p(\vec{x}) \tag{4.7}$$

with

$$h(\vec{x}) = f(\vec{x})/g(\vec{x})$$

and

$$p(\vec{x}) = g(\vec{x})/G$$

Interpreting $p(\vec{x})$ as a probability distribution function we sample M independent points $\vec{x}_1 \ldots \vec{x}_M$ from $p(\vec{x})$ and form the estimate.

$$F_M = GM^{-1} \sum_{i=1}^{M} h(\vec{x}_i) \tag{4.8}$$

which has as expectation value the desired integral F (4.2), while the standard relative error follows as the square root from:

$$(\sigma/F)^2 = (MF/G)^{-1} \int d\vec{x}(h(\vec{x})-F/G)^2 \tag{4.9}$$

With a suitable choice of $g(\vec{x})$ this relative error can be made smaller than that of the crude Monte Carlo estimate. This procedure is called importance sampling, because in sampling with a probability proportional to the known function $g(\vec{x})$ we try *to weight more heavily the regions that contribute much to the* desired integral.

Returning to the Ursell expansion (see table III) it appeared profitable to sample from the Maxwell-Boltzmann momentum distribution function $\varphi(p)$. In that case $3 \cdot 10^4$ points are sufficient to reach an accuracy of a few percent whereas for the conventional numerical integration methods a multiple of this number of points is needed. So to save computing time we have chosen for this weight factor in the Monte Carlo integration. The results of these calculations will be presented in the remainder of this chapter.

a) <u>Incoherent intermediate scattering function.</u>

As already discussed in chapter 2 we expect that the restriction to the two particle collisions in the Ursell expansion is permitted for times smaller than the mean free time τ, which is inversely proportional to the density n. So, to cover a large time scale, it is necessary to consider a system with a small density. It appears that for densities up to $n\sigma^3 \sim 0.1$ the useful time scale is of the same order of magnitude of that reached in neutron scattering experiments, which is the reason that we have only done calculations for densities $n\sigma^3 \leq 0.1$.

Fig. 12 shows the results of the calculations that were carried out for the Ursell expansion and the second derivative expansion of a system with a Lennard-Jones interaction (density $n\sigma^3 = 0.1$, temperature $k_B T/\varepsilon = 1.5$). In fig. 12 are also plotted the results of the molecular dynamics calculations of Michels (1976). One observes that there is an excellent agreement between both the Ursell expansion and the second derivative expansion and the molecular dynamics results, which should be expected because for times smaller than the mean free time τ ($\tau/\sigma(\beta m)^{1/2} \simeq 2$ for $n\sigma^3 = 0.1$) the two particle collisions dominate. Furthermore one sees that the results of the Ursell expansion agree quite well with the results of the second derivative expansion. We note that the calculations in the case of the second derivative expansion are less accurate for large times than in the case of the Ursell expansion because the time integration in (2.58) has to be done over a few number of points (20) to save computing time.

Fig. 13 shows the results of our calculations on a system with a Lennard-Jones interaction with density $n\sigma^3 = 0.1$ and temperature $k_B T/\varepsilon = 1.18$, together with the hard spheres results for this same density. The choice of this point will

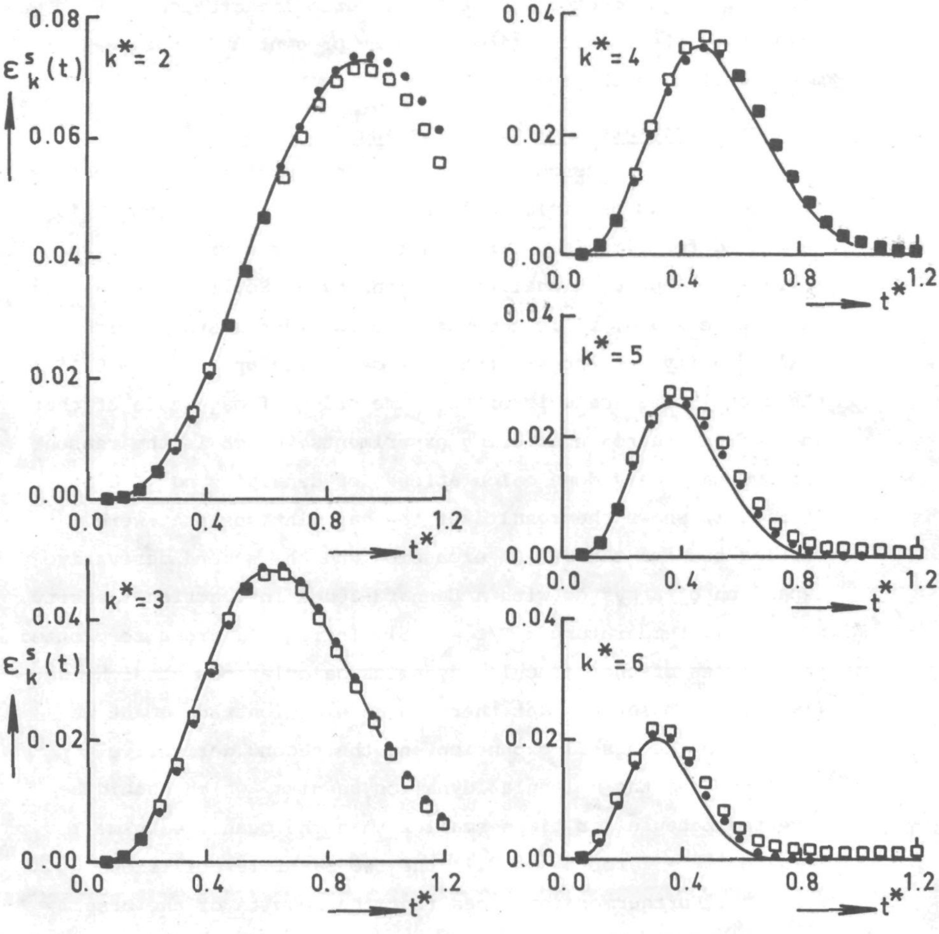


Fig. 12. The incoherent deviation $\varepsilon^s_k(t)$ of a system with a Lennard-Jones interaction; the density $n\sigma^3=0.1$, the reduced temperature $k_BT/\varepsilon=1.5$ ($t^*=t/\sigma(\beta m)^{1/2}$, $k^*=k\sigma$). The circles denote the values obtained by the Ursell expansion, the squares the values of the second derivative expansion while the full line gives the molecular dynamics results (Michels).

be explained at the discussion of the coherent intermediate scattering function. One sees at once that the hard spheres deviation $\varepsilon_k^s(t)$ has qualitatively the same behaviour as the Lennard-Jones interaction but it is a factor 2 smaller in magnitude; apparently the negative part of the Lennard-Jones interaction is very important for a good description of the short time behaviour. A closer inspection of where the contributions come from shows that in particular the region in the potential well contributes heavily.

In fig. 14 the results of our calculations at a lower density $n\sigma^3 = 0.075$ and the same temperature $k_BT/\varepsilon = 1.18$ are plotted. The choice of this density and temperature will also be motivated at the discussion of the coherent function. As to the correspondence between the Ursell and the second derivative expansion in the last two cases, the same remarks as above apply.

Unfortunately there exist at these densities no neutron scattering experiments for the incoherent intermediate scattering function so that it is not possible to compare our theoretical results with experimental data. The lack of neutron data is explained by the fact that only unusual effective scatterers like Ar^{36} allow to perform measurements at these densities. Ar^{36} scatters however coherently. The other candidate would be H_2, but experiments at these low densities are not yet performed.

The behaviour of $F_k^s(t)$ for very short times has to agree with the moments expansion (1.37). Fig. 15 shows the deviation $\varepsilon_k^{s(2)}(t)$ together with the moments expansion up to the fourth moment. It is clear that the moments expansion is only usuful up to times $t/\sigma(\beta m)^{1/2} \simeq 0.1$. This is a consequence of the fact that, due to the hard core, the duration of the collision is small compared with the mean free time.

Finally an interesting feature should be noted. From (3.24) one observes that in the hard spheres Ursell-2 expansion

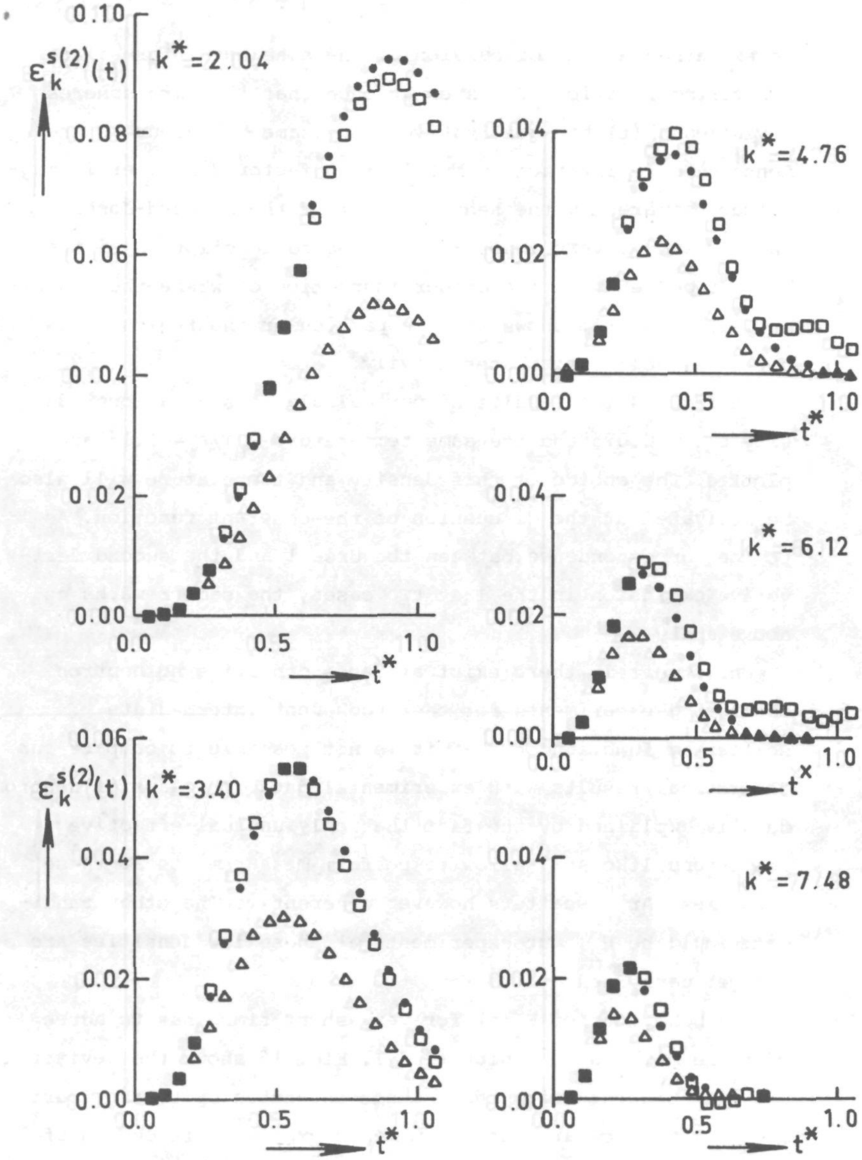


Fig. 13. The incoherent deviation $\varepsilon_k^{s(2)}(t)$ of a Lennard-Jones system with density $n\sigma^3=0.1$ and temperature $k_BT/\varepsilon=1.18$, as calculated with the Ursell expansion (circles) and the second derivative expansion (squares). The triangles represent the hard spheres values for the same density ($k^*=k\sigma$, $t^*=t/\sigma(\beta m)^{1/2}$).

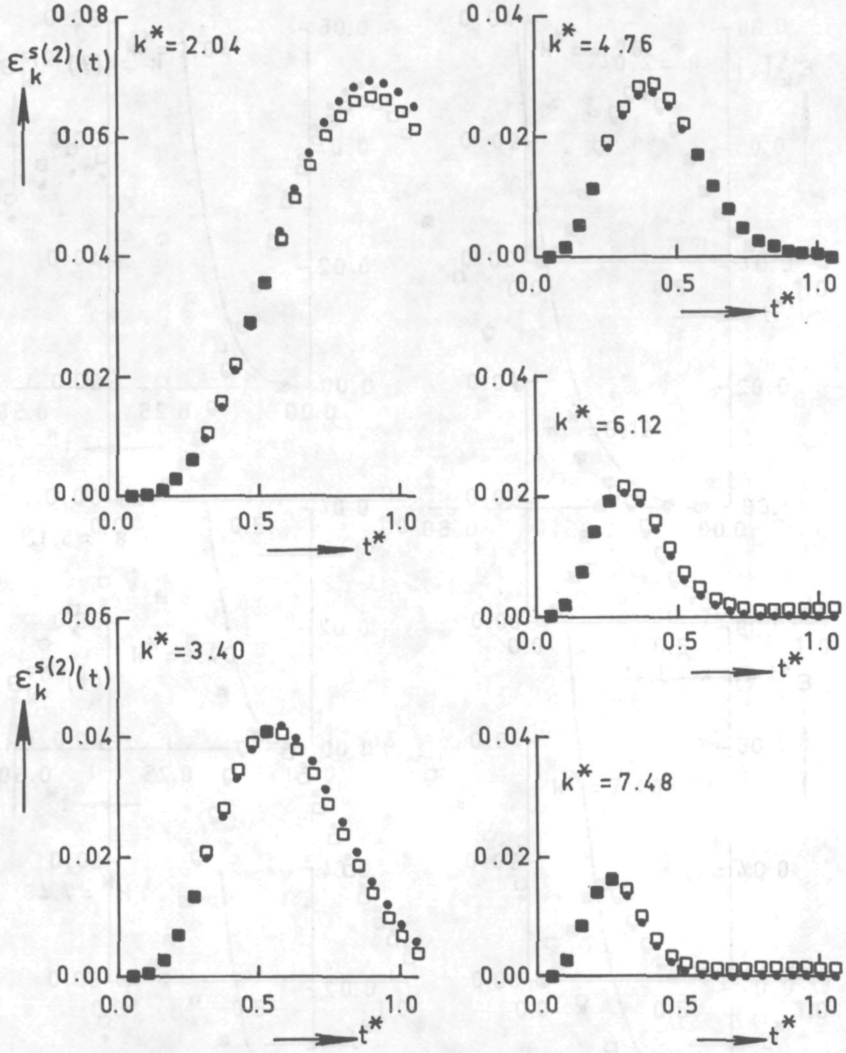


Fig. 14. The incoherent deviation $\varepsilon_k^{s(2)}(t)$ of a Lennard-Jones system with density $n\sigma^3=0.075$ and temperature $k_BT/\varepsilon=1.18$ as obtained by the Ursell expansion (circles) and the second derivative expansion (squares); $k^*=k\sigma$ and $t^*=t/\sigma(\beta m)^{1/2}$.

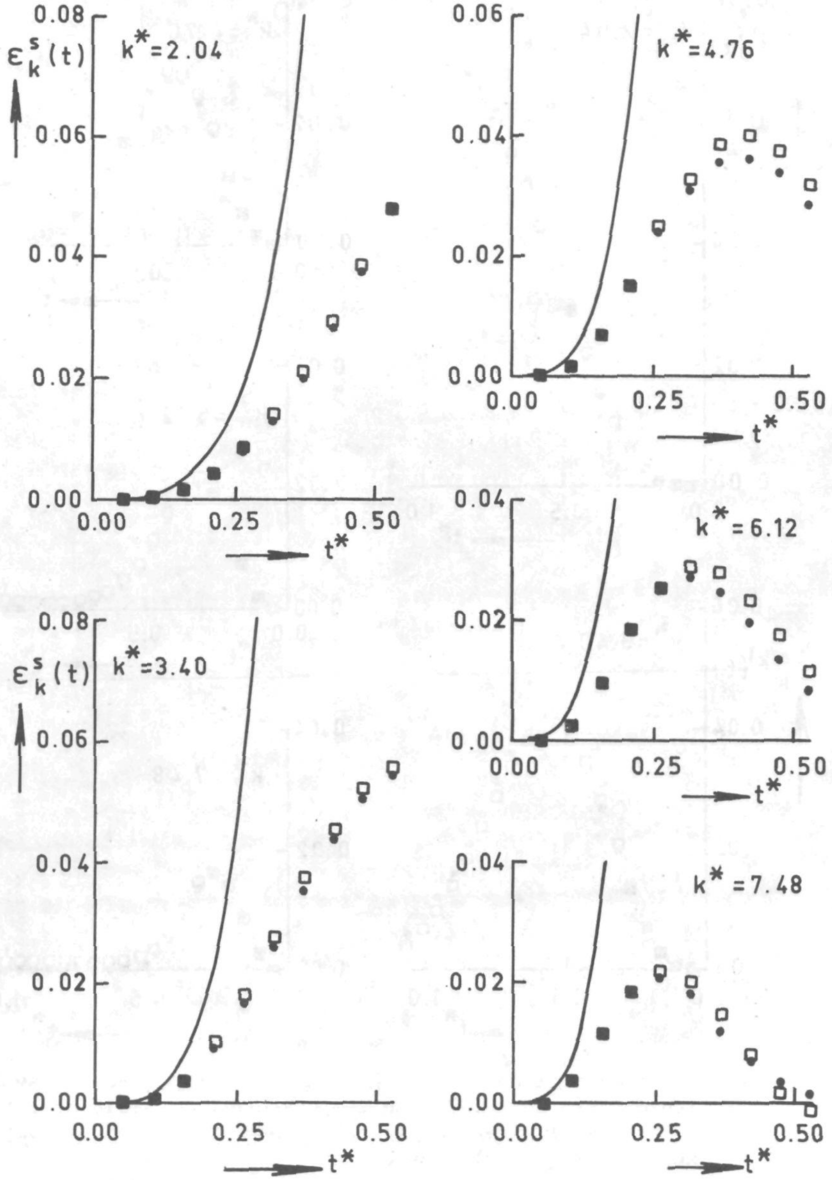


Fig. 15. The incoherent deviation $\varepsilon^s_k(t)$ of a Lennard-Jones system with density $n\sigma^3=0.1$ and temperature $k_BT/\varepsilon=1.18$ as calculated with the Ursell expansion (circles) and the second derivative expansion (squares), compared with the moments expansion (full line); $k^*=k\sigma$ and $t^*=t/\sigma(\beta m)^{1/2}$.

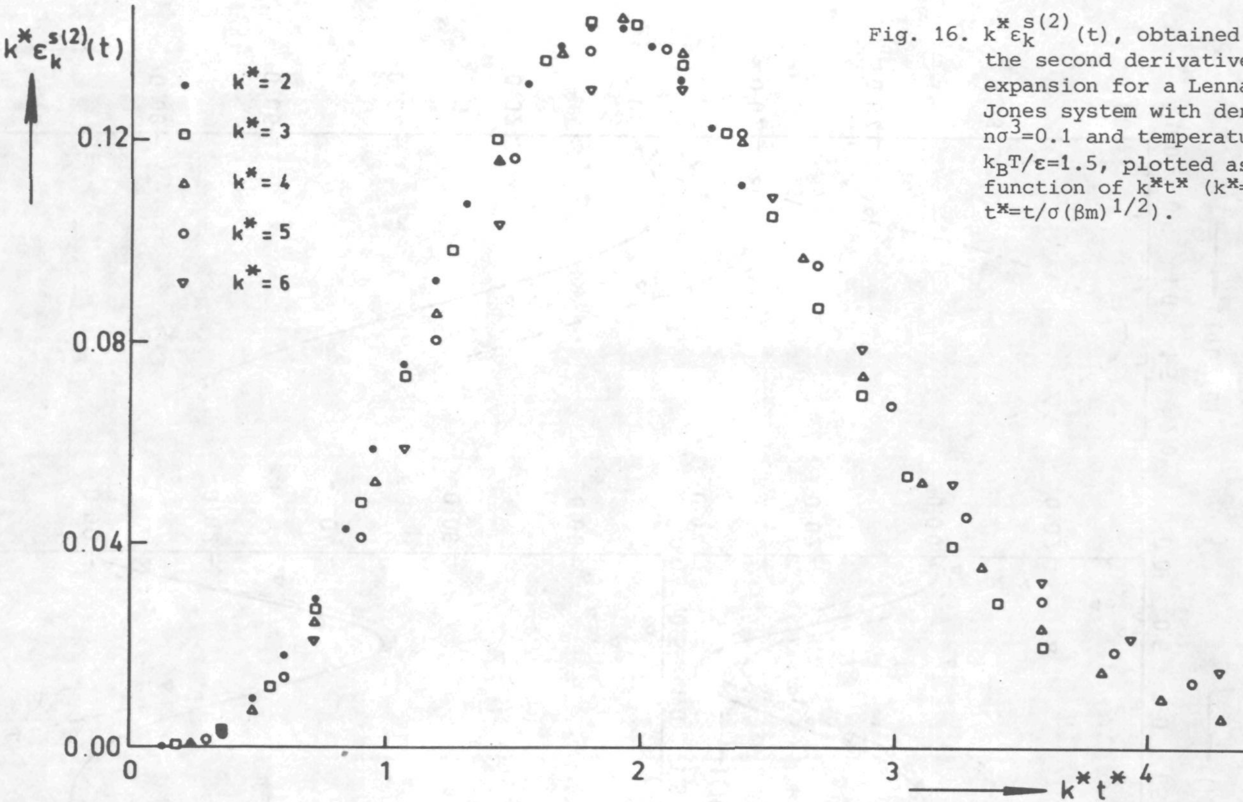


Fig. 16. $k^{*}\varepsilon_k^{s(2)}(t)$, obtained by the second derivative expansion for a Lennard-Jones system with density $n\sigma^3=0.1$ and temperature $k_BT/\varepsilon=1.5$, plotted as a function of $k^{*}t^{*}$ ($k^{*}=k\sigma$, $t^{*}=t/\sigma(\beta m)^{1/2}$).

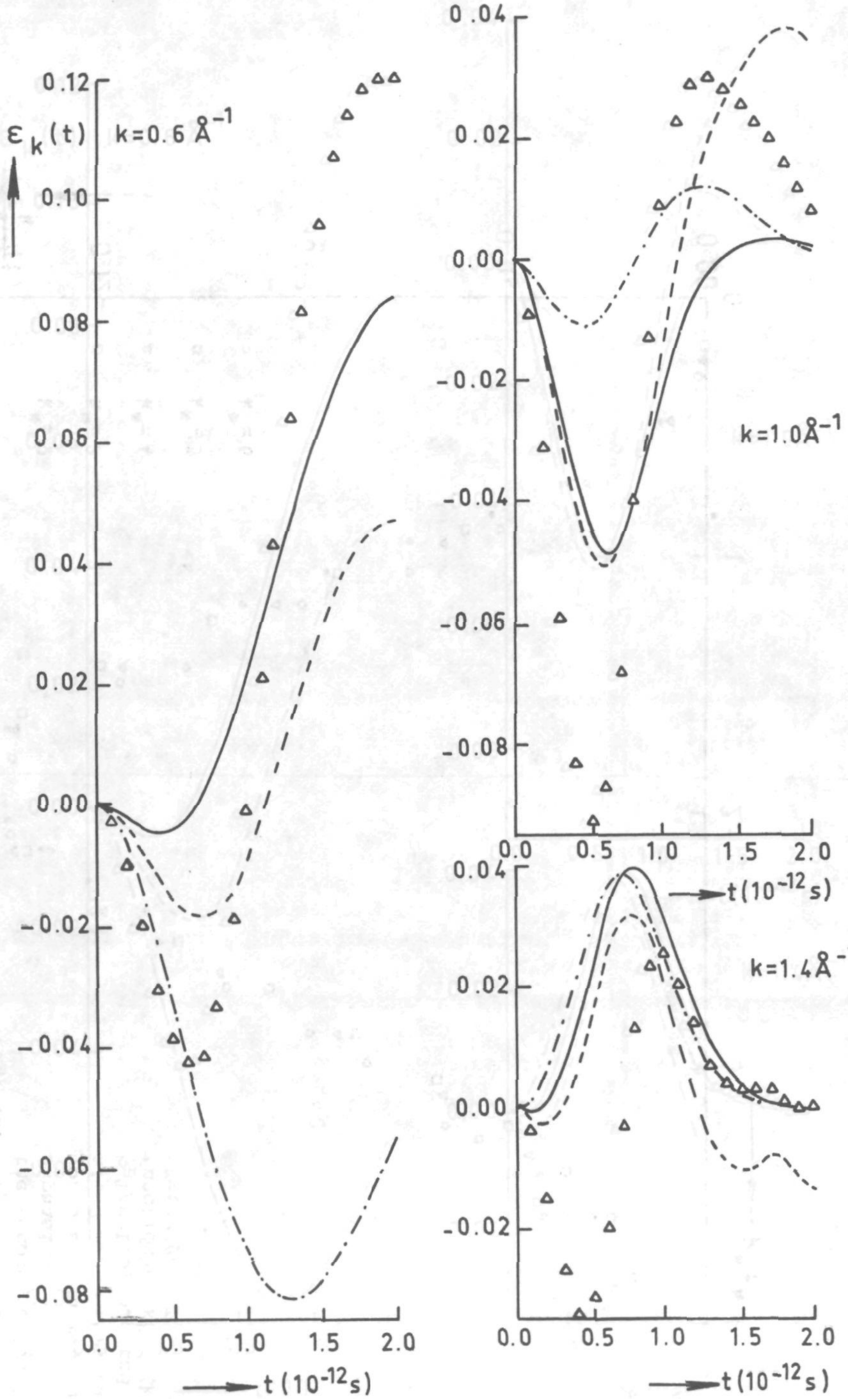


Fig. 17. For the text see page 91.

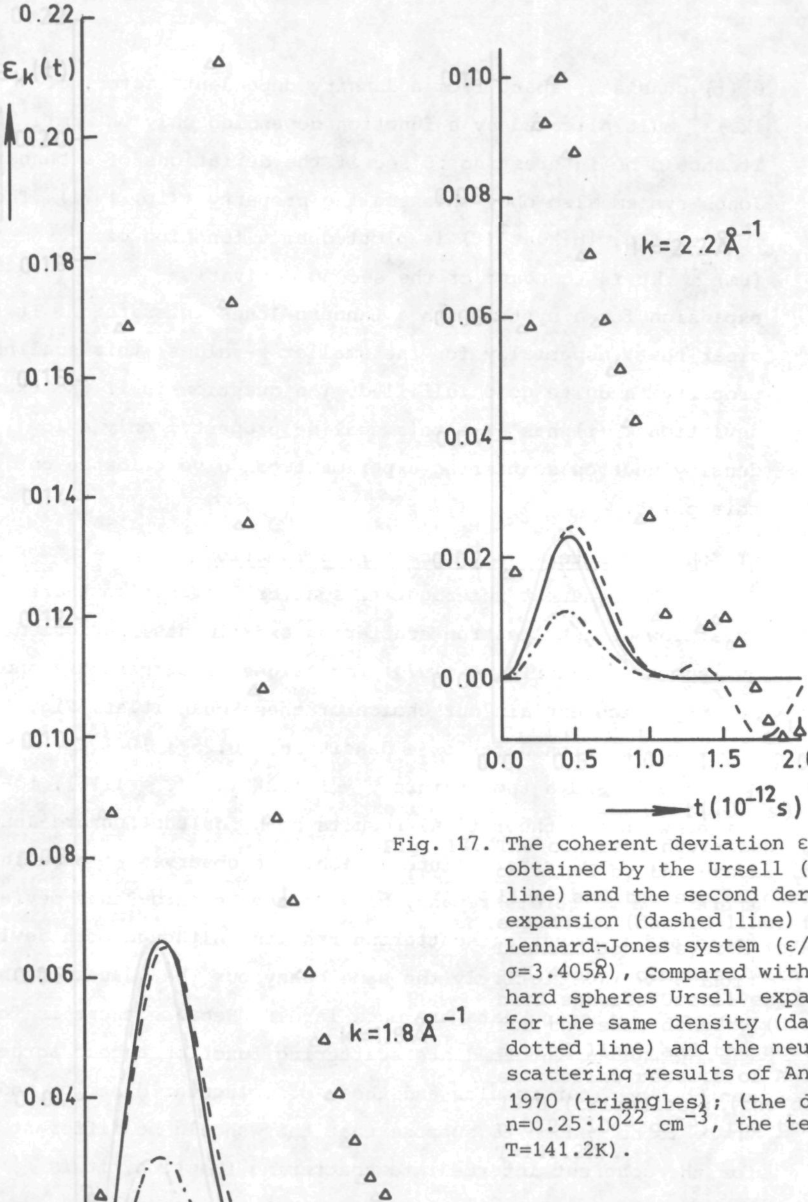


Fig. 17. The coherent deviation $\varepsilon_k(t)$, obtained by the Ursell (full line) and the second derivative expansion (dashed line) for a Lennard-Jones system (ε/k_B=119.8K, σ=3.405Å), compared with the hard spheres Ursell expansion for the same density (dashed-dotted line) and the neutron scattering results of Andriesse, 1970 (triangles); (the density $n=0.25\cdot10^{22}$ cm^{-3}, the temperature T=141.2K).

$\varepsilon_k^s(t)$ consists, apart from a density dependent factor, of $(k\sigma)^{-1}$ multiplicated by a function depending only on $(\beta m)^{-1/2}kt$. It should be interesting to see if the deviations of a Lennard-Jones system also obey this scaling property (Yip, 1971). Therefore in fig. 16 $k\sigma\ \varepsilon_k^s(t)$ is plotted as a function of $(\beta m)^{-1/2}kt$ in the case of the second derivative expansion for a system with a Lennard-Jones interaction. It is clear that, especially for the smaller k-values, this scaling property is quite good fulfilled. The question is if the exact deviation $\varepsilon_k^s(t)$ has also this scaling property; only a low density neutron scattering experiment can give evidence on this point.

b) Coherent intermediate scattering function.

For the coherent intermediate scattering function there exist low density neutron scattering experiments, performed on gaseous Ar^{36} (Andriesse, 1970) for values of temperature and density which explain our choice of these quantities. Fig. 17 shows the neutron data for a density $n = 0.25 \cdot 10^{22}\ cm^{-3}$ ($n\sigma^3 = 0.1$) and a temperature $T = 141.2K$ ($k_BT/\varepsilon = 1.18$), together with the theoretical results both for the Lennard-Jones as for the hard spheres interaction. One observes at once that there is a large discrepancy between the Lennard-Jones deviations and the neutron scattering results. Although both deviations have qualitatively the same behaviour the values of the neutron scattering data are much larger. Because there is for the incoherent intermediate scattering function a good agreement between our results and those of molecular dynamics and there is no reason to suppose that this should be different for the coherent intermediate scattering function, it is difficult to explain the difference between the neutron scattering spectra and our calculations. The neutron data also fail to agree with the moments expansion which applies for very short times; from fig. 18 it appears that there is for these times a good agreement between our results and the moments

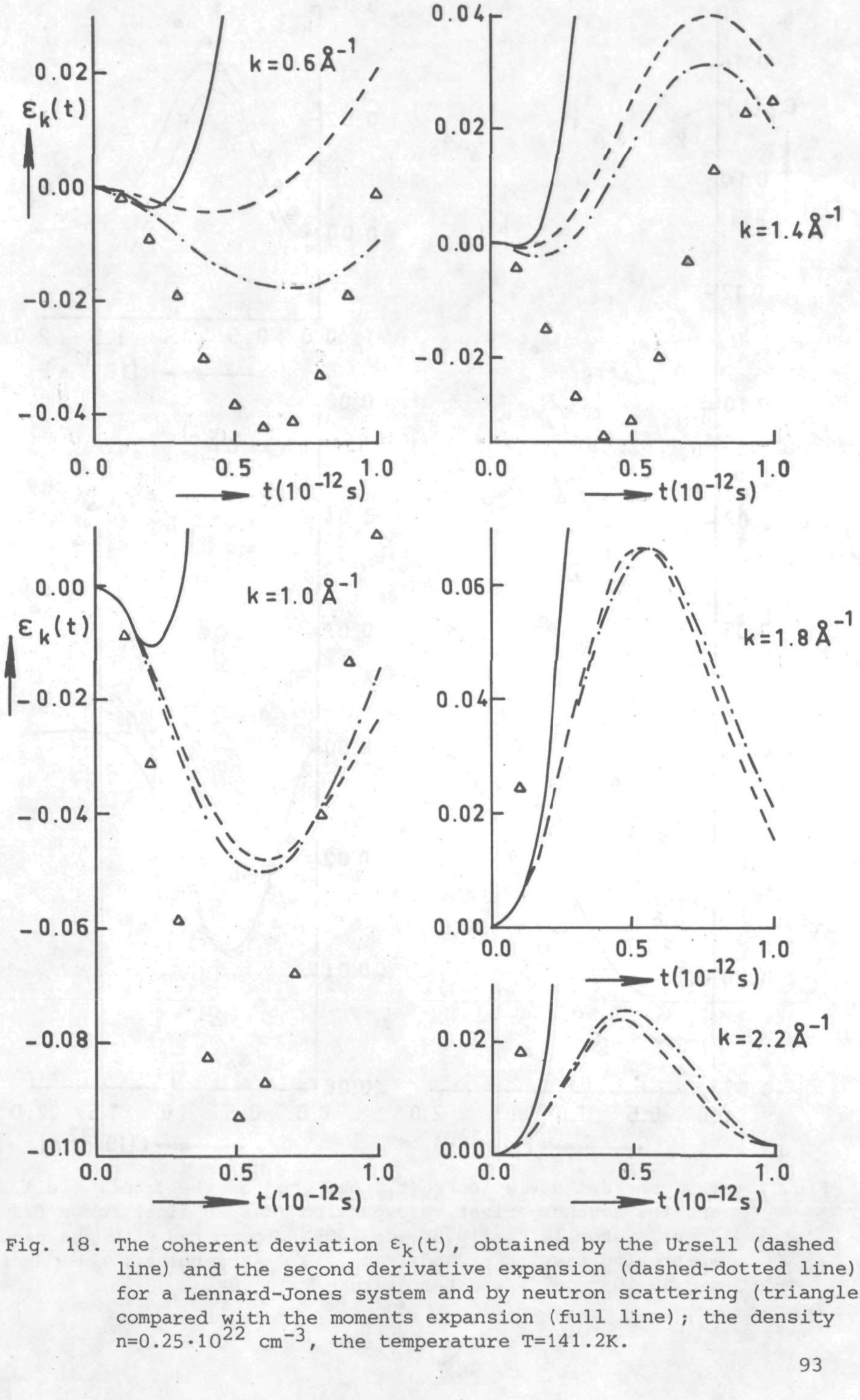


Fig. 18. The coherent deviation $\varepsilon_k(t)$, obtained by the Ursell (dashed line) and the second derivative expansion (dashed-dotted line) for a Lennard-Jones system and by neutron scattering (triangles), compared with the moments expansion (full line); the density $n=0.25\cdot10^{22}$ cm^{-3}, the temperature T=141.2K.

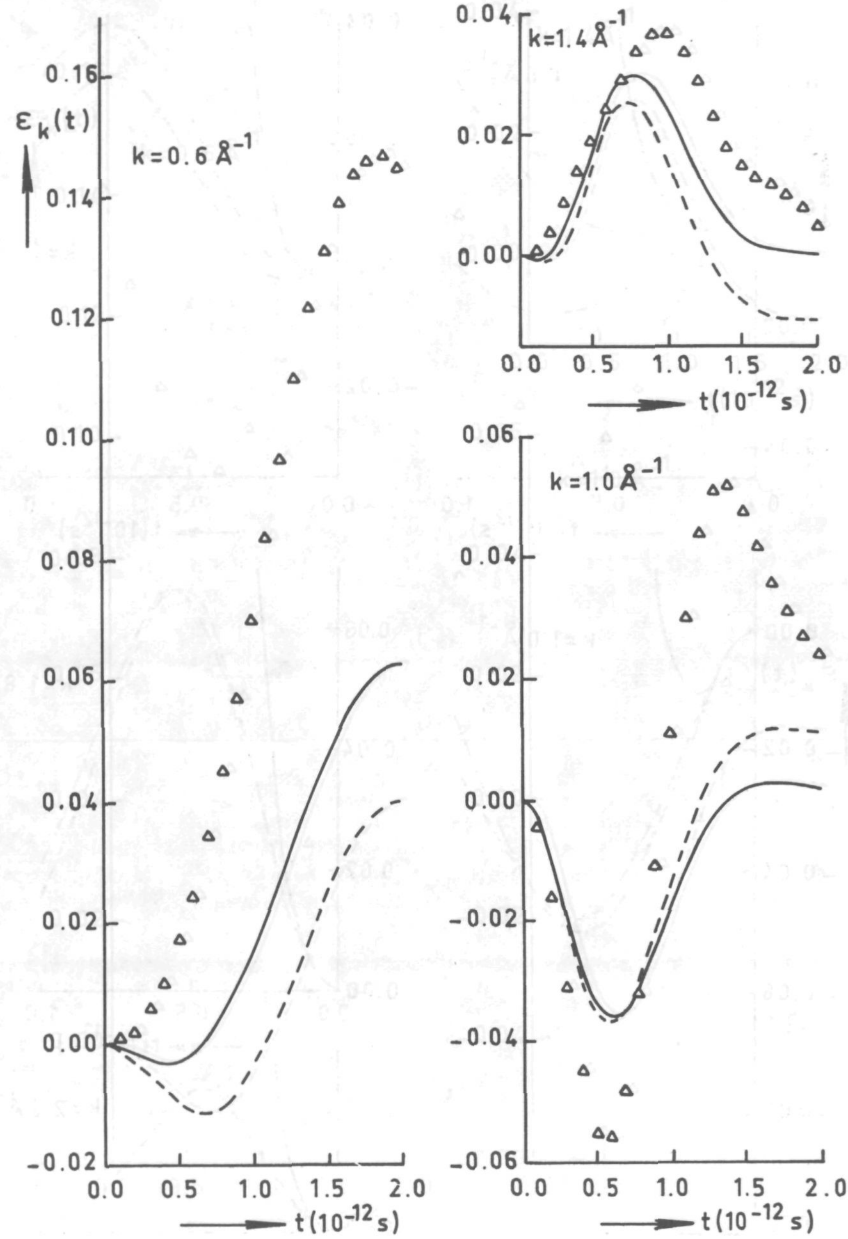


Fig. 19. The coherent deviation $\varepsilon_k(t)$, obtained by the Ursell (full line) and the second derivative expansion (dashed line) for a Lennard-Jones system (ε/k_B=119.8K, σ=3.405Å), compared with the neutron scattering results of Andriesse, 1970 (triangles); the density $n=0.19\cdot10^{22}$ cm^{-3}, the temperature T=141.6K.

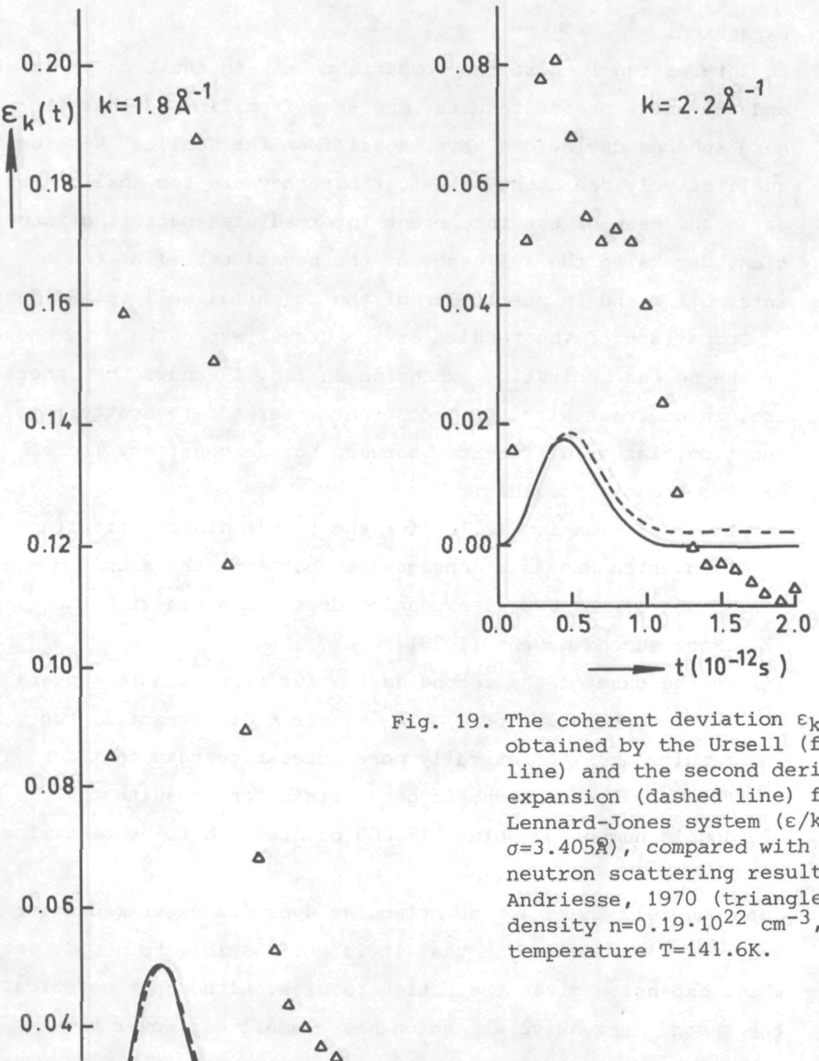


Fig. 19. The coherent deviation $\varepsilon_k(t)$, obtained by the Ursell (full line) and the second derivative expansion (dashed line) for a Lennard-Jones system (ε/k_B=119.8K, σ=3.405Å), *compared with the* neutron scattering results of Andriesse, 1970 (triangles); the density $n=0.19\cdot10^{22}$ cm^{-3}, the temperature T=141.6K.

expansion.

Interesting is also the comparison between the Lennard-Jones and the hard spheres results. One sees from fig. 17 that the hard spheres deviations have, apart from the smallest k-value, qualitatively the right behaviour but they are too small, just as in the case of the incoherent intermediate scattering function. Here also the influence of the negative tail of the interaction and in particular of the potential well is manifest.

Comparison of the results of the Ursell expansion with those of the second derivative expansion in fig. 17 shows that there are, in contrast with the incoherent intermediate scattering function, larger differences between both expansions. There are two reasons for this:

i) the approximation (2.16) for the triple distribution function which has as a consequence that even the second moment (2.36) of the Ursell expansion does not agree with the exact second moment (1.39).

ii) in the case of the second derivative expansion it appears that, especially for $k \sim 1\mathring{A}^{-1}$ where $\varepsilon_k(t)$ is small, the results are statistically more inaccurate than that for the Ursell expansion; to get satisfactory results the double number of points (72000 points) had to be taken for $k = 1\mathring{A}^{-1}$.

Unfortunately there are no molecular dynamics experiments for the coherent function so that it is not possible to decide yet which expansion gives the better results. Although theoretically the second derivative expansion has a small edge over the Ursell expansion we must for the time being take the difference of the two methods as a measure for the accuracy.

In fig. 19 the neutron scattering data for the smaller density $n = 0.19 \cdot 10^{22}\ cm^{-3}$ ($n\sigma^3 = 0.075$) and the temperature $T = 141.6K$ ($k_BT/\varepsilon = 1.18$) are plotted, together with the theoretical results for the Lennard-Jones potential. Although one should expect that for this smaller density the theory would give even better results as in the foregoing case, one

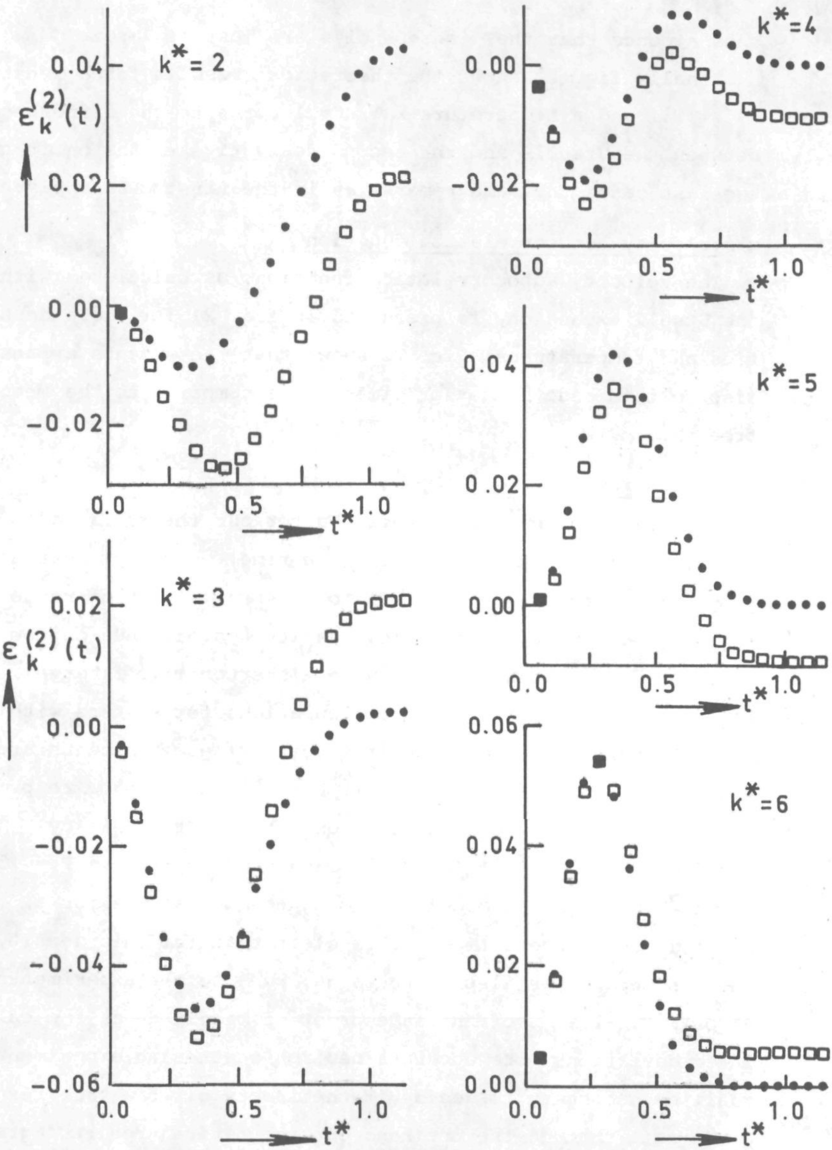


Fig. 20. The coherent deviation $\varepsilon_k^{(2)}(t)$, obtained by the Ursell expansion (circles) and the second derivative expansion (squares) for a Lennard-Jones system with density $n\sigma^3=0.1$ and temperature $k_BT/\varepsilon=1.5$; $k^*=k\sigma$ and $t^*=t/\sigma(\beta m)^{1/2}$.

sees at once that the discrepancies are just as large.

Finally fig. 20 shows the theoretical results for a density $n\sigma^3 = 0.1$ and a temperature $k_BT/\varepsilon = 1.5$. As to the difference between the Ursell- and the second derivative expansion in the two last cases the same remarks as in the first case apply.

c) Velocity autocorrelation function.

The velocity autocorrelation function, as calculated with the Ursell expansion, is presented in fig. 21 for three densities and temperatures. Fig. 22 shows that the moments expansion also in this case holds for times short compared to the mean free time.

d) Discussion.

As earlier discussed in this chapter our theory is valid for times smaller than the mean free time, which is inversely proportional to the density. So to cover a large time range it is necessary to consider low density systems. But on the other hand, if one is content with a shorter time interval, it is also possible to carry out calculations for systems with a higher density, for which neutron scattering experiments are performed on Ar^{36} (Hasman, 1973). Fig. 23 and 24 show resp. the incoherent and coherent neutron data for the density $n = 0.85 \cdot 10^{22}\ cm^{-3}$ ($n\sigma^3 = 0.34$) and the temperature T = 152.7K, together with the theoretically computed deviations for a Lennard-Jones interaction. It is clear that for this density the discrepancy is also quite large. Because the experimental error of 10-15% is of the same order of magnitude as the calculated deviations more accurate neutron scattering experiments shall be necessary to decide if the theory gives a true result.

We note that on the one hand our theoretical results agree quite good with molecular dynamics calculations for times smaller than the mean free time while on the other hand there is a great difference between our results and those of neutron scattering experiments. It should be worthwile to have accurate low density neutron scattering data, both for the coherent

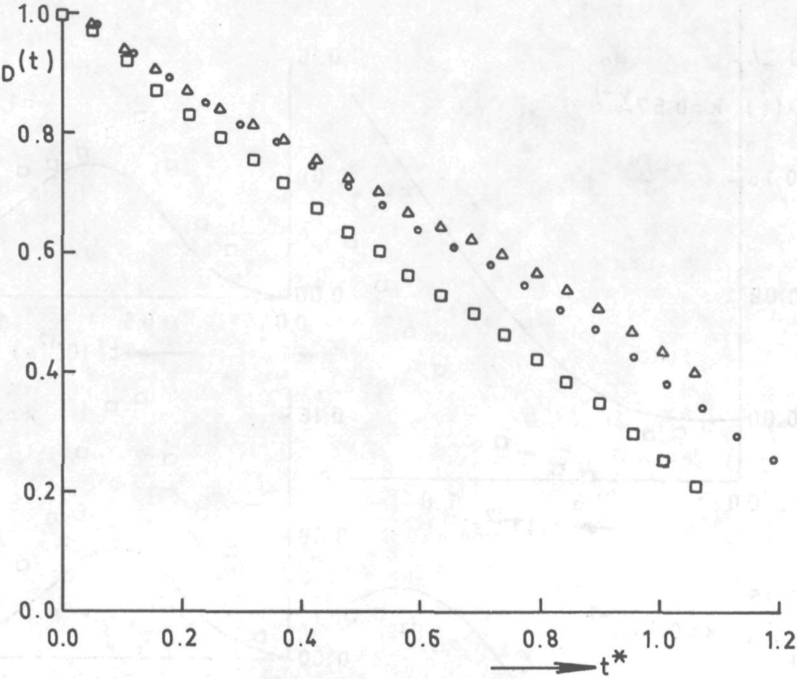


Fig. 21. The velocity autocorrelation function $C_D(t)$, obtained by the Ursell expansion for a Lennard-Jones system with density $n\sigma^3=0.1$ and temperature $k_BT/\varepsilon=1.5$ (circles), $n\sigma^3=0.1$ and $k_BT/\varepsilon= 1.18$ (squares) and $n\sigma^3=0.075$, $k_BT/\varepsilon=1.18$ (triangles); $t^*=t/\sigma(\beta m)^{1/2}$.

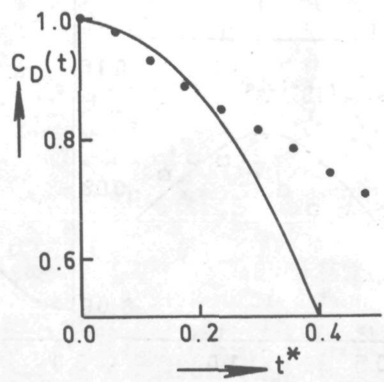


Fig. 22. The velocity autocorrelation function $C_D(t)$, obtained by the Ursell expansion for a Lennard-Jones system with density $n\sigma^3=0.1$ and temperature $k_BT/\varepsilon=1.5$ (circles), compared with the moments expansion (full line); $t^*=t/\sigma(\beta m)^{1/2}$.

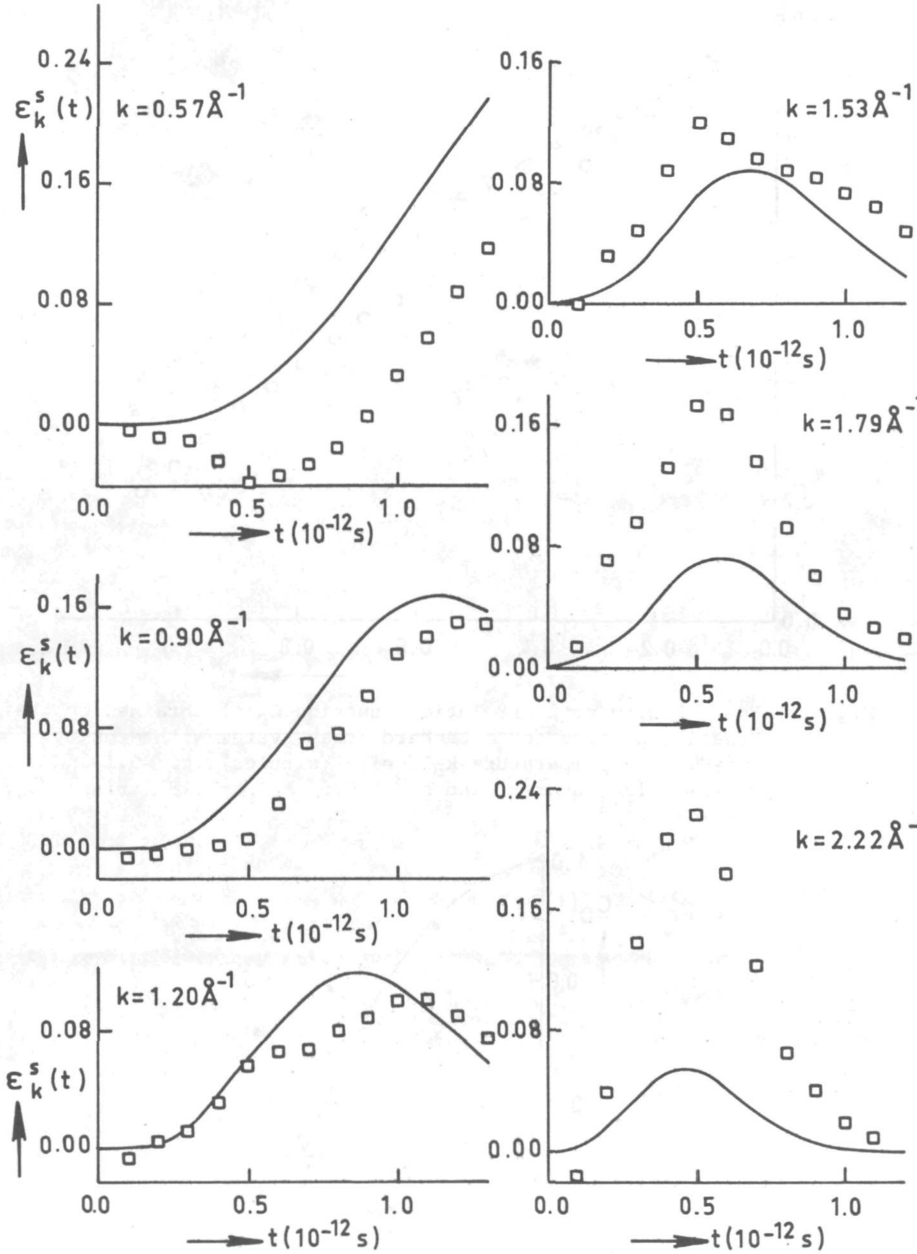


Fig. 23. The incoherent deviation $\varepsilon_k^s(t)$, obtained by the Ursell expansion for a Lennard-Jones system (full line), compared with the neutron scattering results of Hasman, 1973 (squares); the density $n=0.85\cdot10^{22}$ cm^{-3}, the temperature T=152.7K.

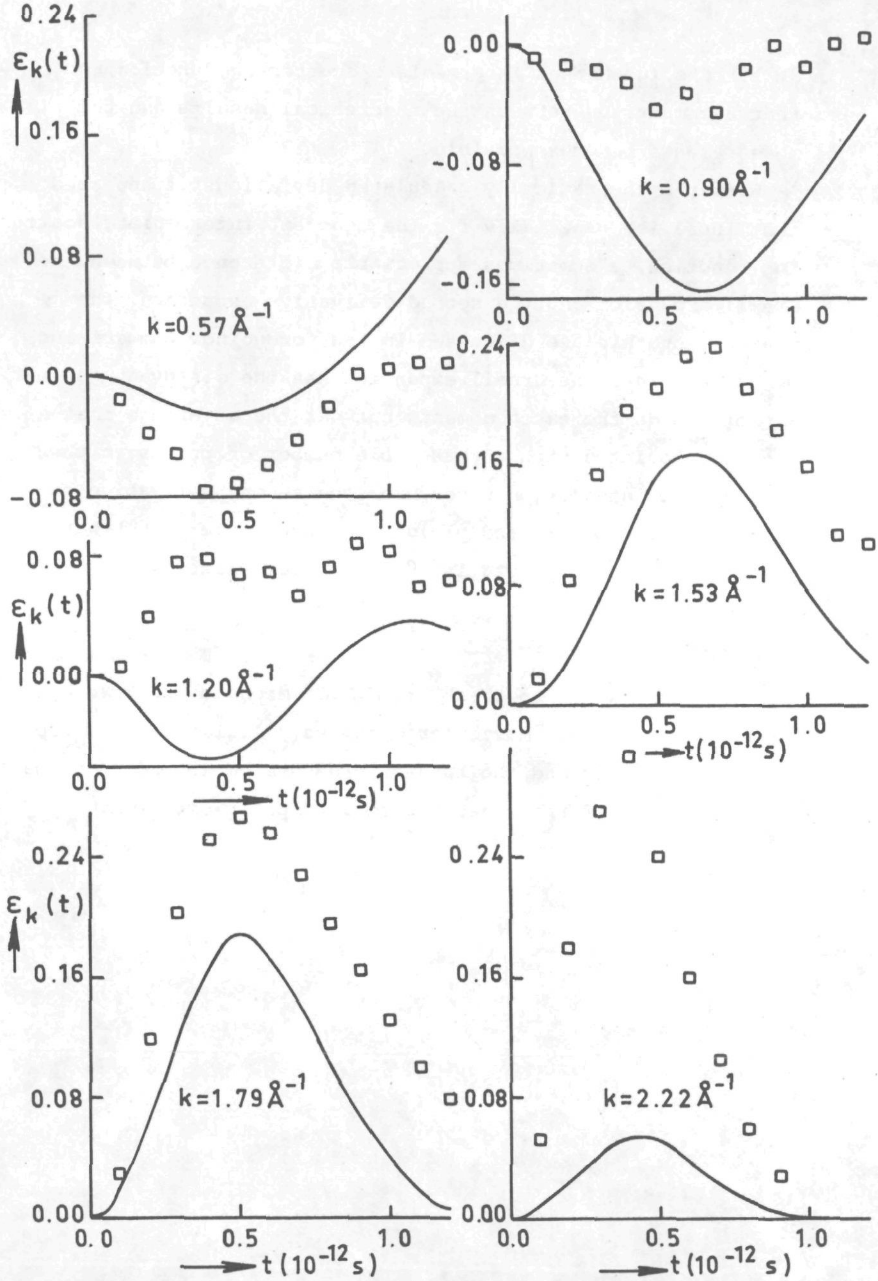


Fig. 24. The coherent deviation $\varepsilon_k(t)$, obtained by the Ursell expansion for a Lennard-Jones system (full line), compared with the neutron scattering results of Hasman, 1973 (squares); the density $n=0.85\cdot10^{22}$ cm^{-3}, the temperature T=152.7K.

as for the incoherent intermediate scattering function, so that a comparison between the theoretical results and the measurements becomes possible.

From the theoretically calculated deviations it appeared that there is, especially for the coherent intermediate scattering function, a sometimes appreciable difference between the Ursell expansion and the second derivative expansion. The reasons for this are discussed in the foregoing. Summarizing we can say that the Ursell expansion has the disadvantage that it not yields the exact moments but has the advantage that it can be calculated with a reasonable number of points in the Monte Carlo integration procedure; the second derivative expansion on the other hand yields the exact moments but has the disadvantage that the statistical accuracy is poor.

Acknowledgement.

The author wants to thank Dr. J.P.J. Michels and J.W. Lyklema for performing their molecular dynamics calculations on resp. the Lennard-Jones and the hard spheres system in order to enable the comparison of this theory with a computer experiment.

APPENDIX A

THE HERMITIAN CONJUGATE OF THE HARD SPHERES PSEUDO LIOUVILLE OPERATOR L_+

The hermitian conjugate $L_+^\dagger$ of the pseudo Liouville operator L_+ is defined in (1.17):

$$<fL_+g> = <gL_+^\dagger f> \tag{A.1}$$

where $f(\Gamma)$ and $g(\Gamma)$ are arbitrary functions of the phase space variables Γ. The operator L_+ is given in (1.21) as:

$$L_+ = L_o + \frac{1}{2} \sum_{i\neq j}\sum T_+(ij) \tag{A.2}$$

Substituting (A.2) in (A.1) one obtains:

$$\begin{aligned} &<f(\Gamma)\ [L_o + \frac{1}{2} \sum_{i\neq j}\sum T_+(ij)]\ g(\Gamma)> \\ &= <g(\Gamma)\ [L_o^\dagger + \frac{1}{2} \sum_{i\neq j}\sum T_+^\dagger(ij)]\ f(\Gamma)> \end{aligned} \tag{A.3}$$

We shall examine the free streaming and the interaction part of this expression separately. Let us denote the free part by $I_o(f,g)$,so

$$I_o(f,g) = <f(\Gamma)L_o g(\Gamma)> \tag{A.4}$$

After substitution of (1.15) this average becomes:

$$\begin{aligned} I_o(f,g) &= <f(\Gamma) \sum_{i=1}^{N} \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{r}_i} g(\Gamma)> \\ &= \int d\Gamma\ \rho(\Gamma) f(\Gamma) \sum_{i=1}^{N} \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{r}_i} g(\Gamma) \end{aligned} \tag{A.5}$$

where use has been made of (1.2). Integrating this once partially one obtains:

$$I_o(f,g) = - \int d\Gamma\ g(\Gamma) \sum_i \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{r}_i} \rho(\Gamma) f(\Gamma) \qquad (A.6)$$

and after working out the derivatives:

$$I_o(f,g) = - \langle g(\Gamma) L_o f(\Gamma) \rangle - \int d\Gamma\ f(\Gamma) g(\Gamma) \sum_i \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{r}_i} \rho(\Gamma) \qquad (A.7)$$

Let us now pay our attention to the second term of this expression. Using the Hamilton function given in (1.1) and the phase space density (1.3) this term can be written for non singular potentials in the following form:

$$\beta \langle f(\Gamma) g(\Gamma) \sum_i \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{r}_i} \frac{1}{2} \sum_{j \neq k} \sum \varphi(r_{jk}) \rangle$$
$$= \beta \langle f(\Gamma) g(\Gamma) \sum_{i \neq j} \sum \left(\frac{\vec{p}_i}{m} \cdot \hat{r}_{ij} \right) \frac{d\varphi(r_{ij})}{dr_{ij}} \rangle$$

One obtains a somewhat other form by interchanging i and j and then adding both expressions:

$$\frac{1}{2} \beta \sum_{i \neq j} \sum \langle f(\Gamma) g(\Gamma) \varphi'(r_{ij}) (\vec{p}_{ij}/m) \cdot \hat{r}_{ij} \rangle$$

with

$$\vec{p}_{ij} = \vec{p}_i - \vec{p}_j$$

This average contains the factor

$$\exp(-\beta\varphi(r_{ij})) \varphi'(r_{ij}) = -\beta^{-1} \frac{d}{dr_{ij}} \exp(-\beta\varphi(r_{ij}))$$

Writing the right hand side for hard spheres as:

$$\frac{d}{dr_{ij}} \theta(r_{ij} - \sigma) = \delta(r_{ij} - \sigma)$$

we come to the following result for hard spheres:

$$\exp(-\beta\varphi(r_{ij}))\varphi'(r_{ij}) = -\beta^{-1}\delta(r_{ij}-\sigma)$$

Now r_{ij} has to be taken at the outside of the sphere, where $\exp(-\beta\varphi(r_{ij})) = 1$, so this factor can again be supplemented and one gets finally for the second term of (A.7):

$$-\frac{1}{2}\sum_{i\neq j}\sum <f(\Gamma)g(\Gamma)\delta(r_{ij}-\sigma)(\vec{p}_{ij}/m)\cdot\hat{r}_{ij}>$$

With (A.7) the following expression is obtained:

$$\begin{aligned} <f(\Gamma)L_o g(\Gamma)> &= -<g(\Gamma)L_o f(\Gamma)> \\ &\quad -<g(\Gamma)\ \frac{1}{2}\sum_{i\neq j}\sum\ \delta(r_{ij}-\sigma)(\vec{p}_{ij}/m)\cdot\hat{r}_{ij}f(\Gamma)> \end{aligned} \qquad (A.8)$$

So the hermitian conjugate $L_o^\dagger$ of the free streaming part of the pseudo Liouville operator L_+ is:

$$L_o^\dagger = -L_o - \frac{1}{2}\sum_{i\neq j}\sum\ \delta(r_{ij}-\sigma)(\vec{p}_{ij}/m)\cdot\hat{r}_{ij} \qquad (A.9)$$

The second term in (A.3), the interaction part, will be denoted by I'(f,g):

$$I'(f,g) = <f(\Gamma)\ \frac{1}{2}\sum_{i\neq j}\sum\ T_+(ij)g(\Gamma)> \qquad (A.10)$$

This becomes after substitution of (1.22):

$$\begin{aligned} I'(f,g) &= \int d\Gamma\ \rho(\Gamma)f(\Gamma)\frac{1}{2}\sum_{i\neq j}\sum|\vec{v}_{ij}\cdot\hat{r}_{ij}|\theta(-\vec{v}_{ij}\cdot\vec{r}_{ij})\delta(r_{ij}-\sigma) \\ &\qquad (b_{ij}-1)g(\Gamma) \qquad (A.11) \\ &= \frac{1}{2}\sum_{i\neq j}\sum\int d\Gamma\ \rho(\Gamma)f(..,\vec{p}_i,..,\vec{p}_j,..)|\vec{v}_{ij}\cdot\hat{r}_{ij}|\theta(-\vec{v}_{ij}\cdot\vec{r}_{ij}) \\ &\qquad \delta(r_{ij}-\sigma)\ [g(..,\vec{p}_i',..,\vec{p}_j',..)-g(..,\vec{p}_i,..,\vec{p}_j,..)] \end{aligned}$$

where use has been made of (1.24) and (1.25). In the first term of (A.11) we make a change of variables from $\vec{p}_i,\vec{p}_j$ to $\vec{p}_i',\vec{p}_j'$. The element of phase space $d\Gamma$ and the phase space density function $\rho(\Gamma)$ are invariant under this transformation from Γ to Γ'. So $d\Gamma = d\Gamma'$ and $\rho(\Gamma) = \rho(\Gamma')$. Furthermore

$$\vec{p}_{ij}' \cdot \vec{r}_{ij} = -\vec{p}_{ij} \cdot \vec{r}_{ij} \tag{A.12}$$

as can easily be verified with (1.25). After this transformation we obtain for the first term of (A.11):

$$\frac{1}{2}\sum_{i\neq j}\sum \int d\Gamma' \rho(\Gamma')f(..,\vec{p}_i'-(\vec{p}_{ij}'\cdot\hat{r}_{ij})\hat{r}_{ij},..,\vec{p}_j'+(\vec{p}_{ij}'\cdot\hat{r}_{ij})\hat{r}_{ij},..)$$

$$|-\vec{v}_{ij}'\cdot\hat{r}_{ij}|\theta(\vec{v}_{ij}'\cdot\vec{r}_{ij})\delta(r_{ij}-\sigma)g(..,\vec{p}_i',..,\vec{p}_j',..)$$

and after omitting the primes and again introducing the collision operator b_{ij}:

$$\frac{1}{2}\sum_{i\neq j}\sum \int d\Gamma \rho(\Gamma)g(\Gamma)|\vec{v}_{ij}\cdot\hat{r}_{ij}|\theta(\vec{v}_{ij}\cdot\vec{r}_{ij})\delta(r_{ij}-\sigma)b_{ij}f(\Gamma)$$

So the collision term $I'(f,g)$ becomes:

$$\begin{aligned} I'(f,g) &= \langle g(\Gamma)\frac{1}{2}\sum_{i\neq j}\sum|\vec{v}_{ij}\cdot\hat{r}_{ij}|\theta(\vec{v}_{ij}\cdot\vec{r}_{ij})\delta(r_{ij}-\sigma)b_{ij}f(\Gamma)\rangle \\ &- \langle g(\Gamma)\frac{1}{2}\sum_{i\neq j}\sum|\vec{v}_{ij}\cdot\hat{r}_{ij}|\theta(-\vec{v}_{ij}\cdot\vec{r}_{ij})\delta(r_{ij}-\sigma)f(\Gamma)\rangle \end{aligned} \tag{A.13}$$

and one sees immediately that the hermitian conjugate $T_+^\dagger(ij)$ of $T_+(ij)$ is:

$$\begin{aligned} T_+^\dagger(ij) &= |\vec{v}_{ij}\cdot\hat{r}_{ij}|\theta(\vec{v}_{ij}\cdot\vec{r}_{ij})\delta(r_{ij}-\sigma)b_{ij} \\ &- |\vec{v}_{ij}\cdot\hat{r}_{ij}|\theta(-\vec{v}_{ij}\cdot\vec{r}_{ij})\delta(r_{ij}-\sigma) \end{aligned} \tag{A.14}$$

The first term on the right hand side looks very similar to the expression (1.22) for $T_-(ij)$. This suggests that we can write (A. 14) in the following form:

$$T_+^\dagger(ij) = T_-(ij)+|\vec{v}_{ij}\cdot\hat{r}_{ij}|\delta(r_{ij}-\sigma)[\theta(\vec{v}_{ij}\cdot\vec{r}_{ij})-\theta(-\vec{v}_{ij}\cdot\vec{r}_{ij})] \quad (A.15)$$

which is easily seen to be the same as:

$$\begin{aligned} T_+^\dagger(ij) &= T_-(ij) + (\vec{v}_{ij}\cdot\hat{r}_{ij})\delta(r_{ij}-\sigma) \\ &= T_-(ij) + \vec{p}_{ij}/m \cdot \hat{r}_{ij}\ \delta(r_{ij}-\sigma) \end{aligned} \quad (A.16)$$

With (A.3), (A.9), (A. 16) and (1.21) one obtains finally for the hermitian conjugate $L_+^\dagger$:

$$\begin{aligned} L_+^\dagger &= L_o^\dagger + \frac{1}{2}\sum_{i\neq j}\sum T_+^\dagger(ij) \\ &= -L_o + \frac{1}{2}\sum_{i\neq j}\sum T_-(ij) = -L_- \end{aligned} \quad (A.17)$$

APPENDIX B

THE CALCULATION OF THE EXACT HARD SPHERES MOMENTS

From (1.36), (1.37) and (1.44) one sees that the n'th moment $M_n(k)$ of the intermediate scattering function can be written as:

$$M_n(k) = N^{-1}\langle\sum_i \exp(-i\vec{k}.\vec{r}_i)(L_+)^n \sum_j \exp(i\vec{k}.\vec{r}_j)\rangle \qquad (B.1)$$

In an analogous way the moments of the incoherent intermediate scattering function are obtained as:

$$M_n^s(k) = N^{-1}\langle\sum_i \exp(-i\vec{k}.\vec{r}_i)(L_+)^n \exp(i\vec{k}.\vec{r}_i)\rangle \qquad (B.2)$$

So it follows from (B.1) and (B.2) that:

$$M_n(k) = M_n^s(k) + N^{-1}\langle\sum_{i\neq j}\sum \exp(-i\vec{k}.\vec{r}_i)(L_+)^n \exp(i\vec{k}.\vec{r}_j)\rangle \qquad (B.3)$$

and calling the i'th and j'th particle particle 1 and 2 resp. the summation yields merely a factor N(N-1):

$$M_n(k) = M_n^s(k)+(N-1)\langle\exp(-i\vec{k}.\vec{r}_1)(L_+)^n \exp(i\vec{k}.\vec{r}_2)\rangle \qquad (B.4)$$

One should take care of the sequence of the operators in (B.1)-(B.4), because L_o and $T_\pm$ do not commute.
We shall now give a derivation of the first few moments.

a) Zeroth moment

$$M_o^s(k) = N^{-1}\langle\sum_i \exp(-i\vec{k}.\vec{r}_i)\exp(i\vec{k}.\vec{r}_i)\rangle = 1 \qquad (B.5)$$

Thus with (B.4) the zeroth moment of $F_k(t)$ becomes:

$$M_o(k) = 1 + (N-1)\langle\exp(-i\vec{k}\cdot(\vec{r}_1-\vec{r}_2))\rangle$$

From (1.5) and (1.9) this is easily seen the same as:

$$M_o(k) = 1 + n\tilde{G}(k) = S(k) \tag{B.6}$$

b) First moment

The first moment $M_1^s(k)$ of the incoherent intermediate scattering function follows from (B.2) and (1.21) as:

$$M_1^s(k) = N^{-1}\langle\sum_i \exp(-i\vec{k}.\vec{r}_i)[L_o + \frac{1}{2}\sum_{i\neq j}\sum T_+(ij)] \exp(i\vec{k}.\vec{r}_i)\rangle \tag{B.7}$$

One observes immediately that in (B.7) the operator $T_+(ij)$ works only on a function of the space variables and therefore gives a contribution zero because of the presence of the operator $(b_{ij}-1)$ in $T_+(ij)$ (see (1.22) and (1.24)). Thus:

$$M_1^s(k) = N^{-1}\langle\sum_i \exp(-i\vec{k}.\vec{r}_i)\, L_o \exp(i\vec{k}.\vec{r}_i)\rangle$$

and after the substitution of L_o from (1.15) this expression becomes:

$$M_1^s(k) = N^{-1}\langle\sum_i \exp(-i\vec{k}.\vec{r}_i)\sum_j \frac{\vec{p}_j}{m}\cdot\frac{\partial}{\partial\vec{r}_j}\exp(i\vec{k}.\vec{r}_i)\rangle$$

$$= N^{-1}\langle\sum_i i\vec{k}.\vec{p}_i/m\rangle$$

This is an average of an odd power of the momentum so the first moment of $F_k^s(t)$ is zero:

$$M_1^s(k) = 0 \tag{B.8}$$

The first moment of $F_k(t)$ follows from (B.4) and (B.8) as:

$$M_1(k) = (N-1)\langle\exp(-i\vec{k}.\vec{r}_1)L_+ \exp(i\vec{k}.\vec{r}_2)\rangle$$

In the same way as for the self function one arrives at:

$$M_1(k) = (N-1)<(i\vec{k}.\vec{p}_2/m)\exp(-i\vec{k}.(\vec{r}_1-\vec{r}_2))>$$

and because we have here also an odd power of the momentum we find finally:

$$M_1(k) = 0 \tag{B.9}$$

c) <u>Second moment</u>

The second moment of $F_k^s(t)$ follows from (B.2) as:

$$M_2^s(k) = N^{-1}<\sum_i \exp(-i\vec{k}.\vec{r}_i)(L_+)^2\exp(i\vec{k}.\vec{r}_i)>$$

Here we can simplify the computation by making use of the hermitian conjugate $L_+^\dagger$ of L_+, defined in (1.17) and (1.26) to obtain:

$$M_2^s(k) = N^{-1}<\sum_i[-L_- \exp(-i\vec{k}.\vec{r}_i)][L_+ \exp(i\vec{k}.\vec{r}_i)]>$$

The operators $T_\pm(ij)$ that are contained in the pseudo Liouville operators $L_\pm$ (1.21) give again a zero result because of the presence of $(b_{ij}-1)$, so we get:

$$\begin{aligned} M_2^s(k) &= N^{-1}<\sum_i[-L_o \exp(-i\vec{k}.\vec{r}_i)][L_o \exp(i\vec{k}.\vec{r}_i)]> \\ &= -N^{-1}<\sum_i(\vec{k}.\vec{p}_i/m)^2> = -k^2/\beta m \end{aligned} \tag{B.10}$$

The expressions (B.4) with n = 2 and (B.10) yield for the second moment of $F_k(t)$:

$$M_2(k) = -k^2/\beta m+(N-1)<\exp(-i\vec{k}.\vec{r}_1)(L_+)^2\exp(i\vec{k}.\vec{r}_2)>$$

Shifting one of the L_+ operators to the left and proceeding in the same way as for $M_2^s(k)$ we find:

$$M_2(k) = -k^2/\beta m-(N-1)<(\vec{k}.\vec{p}_1/m)(\vec{k}.\vec{p}_2/m)\exp(-i\vec{k}.(\vec{r}_1-\vec{r}_2))>$$

Again the average over the momenta is zero, so

$$M_2(k) = -k^2/\beta m \tag{B.11}$$

d) Third moment

From (B.2) one sees that the third moment of the incoherent intermediate scattering function can be written as:

$$M_3^s(k) = N^{-1}<\sum_i \exp(-i\vec{k}.\vec{r}_i)(L_+)^3 \exp(i\vec{k}.\vec{r}_i)>$$

We can choose particle i as particle 1, so the sum over i produces merely a factor N. Furthermore one Liouville operator L_+ may be shifted to the left, yielding:

$$M_3^s(k) = <[-L_- \exp(-i\vec{k}.\vec{r}_1)]L_+[L_+ \exp(i\vec{k}.\vec{r}_1)]>$$

Because only the free streaming parts L_o in the Liouville operators $L_\pm$ (1.21) give a nonzero contribution if they work on a function of the coordinates only, this expression takes the following form:

$$M_3^s(k) = -<[L_o \exp(-i\vec{k}.\vec{r}_1)]L_+[L_o \exp(i\vec{k}.\vec{r}_1)]>$$

$$= -<(\vec{k}.\vec{p}_1/m)\exp(-i\vec{k}.\vec{r}_1)[L_o + \frac{1}{2}\sum_{i\neq j}\sum T_+(ij)]$$

$$(\vec{k}.\vec{p}_1/m)\exp(i\vec{k}.\vec{r}_1)> \tag{B.12}$$

One observes at once that the free streaming part L_o gives a contribution $-i<(\vec{k}.\vec{p}_1/m)^3>$ and this is zero because it is an average over an odd power of the momentum. The operator $T_+(ij)$ yields only a finite contribution if the pair (ij) contains particle 1.

For the other particle we can take particle 2, so the summation produces only a factor (N-1) and we get for the third moment M_3^s:

$$M_3^s(k) = -(N-1)\langle(\vec{k}.\vec{p}_1/m)\exp(-i\vec{k}.\vec{r}_1)T_+(12)(\vec{k}.\vec{p}_1/m)\exp(i\vec{k}.\vec{r}_1)\rangle \tag{B.13}$$

From (1.22) and (1.24) it follows that:

$$T_+(12)\vec{k}.\vec{p}_1/m = |\vec{p}_{12}.\hat{r}_{12}/m|\Theta(-\vec{p}_{12}.\vec{r}_{12})\delta(r_{12}-\sigma)$$

$$(\vec{k}.\vec{p}_1'/m - \vec{k}.\vec{p}_1/m)$$

With (1.25) this expression can be rewritten as:

$$T_+(12)\vec{k}.\vec{p}_1/m = (\vec{p}_{12}\cdot\hat{r}_{12}/m)^2(\vec{k}\cdot\hat{r}_{12})\Theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma) \tag{B.14}$$

Substituting (B.14) in (B.13) we obtain:

$$M_3^s(k) = -(N-1)\langle(\vec{k}\cdot\vec{p}_1/m)(\vec{k}.\hat{r}_{12})(\vec{p}_{12}\cdot\hat{r}_{12}/m)^2$$

$$\Theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)\rangle$$

Interchanging the indices 1 and 2 the factor $(\vec{k}.\vec{p}_1/m)(\vec{k}.\hat{r}_{12})$ goes over in $-(\vec{k}.\vec{p}_2/m)(\vec{k}.\hat{r}_{12})$ and if we add both expressions we come to:

$$M_3^s(k) = -\frac{1}{2}(N-1)\langle(\vec{k}.\vec{p}_{12}/m)(\vec{k}.\hat{r}_{12})(\vec{p}_{12}\cdot\hat{r}_{12}/m)^2$$

$$\Theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)\rangle$$

The ensemble average can be written out as:

$$M_3^s(k) = -n^2/(2N) \int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \exp(-\beta(p_1^2+p_2^2)/2m) g(r_{12})$$

$$(\vec{k}.\vec{p}_{12}/m)(\vec{k}.\hat{r}_{12})(\vec{p}_{12}\cdot\hat{r}_{12}/m)^2 \Theta(-\vec{p}_{12}.\vec{r}_{12})\delta(r_{12}-\sigma)$$

$$\cdot \left[\int d\vec{p}_1 d\vec{p}_2 \exp(-\beta(p_1^2+p_2^2)/2m)\right]^{-1}$$

where use has been made of (1.5)-(1.7).

We now make a transformation to the center of mass coordinates $\vec{R}$ and momenta $\vec{P}$ and to the relative coordinates $\vec{r}$ and momenta $\vec{p}$, defined by:

$$\vec{P} = \vec{p}_1+\vec{p}_2 \qquad \vec{R} = (\vec{r}_1+\vec{r}_2)/2$$
$$\vec{p} = (\vec{p}_1-\vec{p}_2)/2 \qquad \vec{r} = \vec{r}_1-\vec{r}_2 \tag{B.15}$$

After this transformation the integral becomes:

$$M_3^s(k) = -n^2/(2N) \int d\vec{R}d\vec{r}d\vec{P}d\vec{p} \exp(-\beta(P^2/4+p^2)/m) g(r)$$

$$(\vec{k}.2\vec{p}/m)(\vec{k}.\hat{r})(2\vec{p}.\hat{r}/m)^2\Theta(-\vec{p}\cdot\vec{r})\delta(r-\sigma) \cdot$$

$$\left[\int d\vec{P}d\vec{p} \exp(-\beta(P^2/4+p^2)/m)\right]^{-1}$$

The integration over $\vec{R}$ yields only a factor V, that over $\vec{P}$ in the numerator and denominator cancel and the integral over $\vec{p}$ in the denominator gives a factor $(\pi m/\beta)^{3/2}$ so we get for the third moment:

$$M_3^s(k) = -\frac{1}{2}n\ (\beta/\pi m)^{\frac{3}{2}} \int d\vec{r}d\vec{p} \exp(-\beta p^2/m) g(r)$$
$$(\vec{k}\cdot 2\vec{p}/m)(\vec{k}\cdot\hat{r})(2\vec{p}.\hat{r}/m)^2\Theta(-\vec{p}\cdot\vec{r})\delta(r-\sigma) \tag{B.16}$$

We start with the calculation of the $\vec{p}$-integral:

$$\int d\vec{p}\ \exp(-\beta p^2/m)(\vec{k}\cdot 2\vec{p}/m)(\hat{r}\cdot 2\vec{p}/m)^2\Theta(-\vec{p}\cdot\vec{r})$$

If we take $\hat{r}$ as the polar axis and go over to spherical coordinates (p,θ,φ) the integral becomes:

$$\int_0^\infty p^2 dp \int_0^\pi \sin\theta\ d\theta \int_0^{2\pi} d\varphi\ \exp(-\beta p^2/m)(\vec{k}\cdot 2\vec{p}/m)(2p\cos\theta/m)^2\Theta(-pr\cos\theta)$$

The step function $\Theta(-pr\cos\theta)$ reduces the interval of the θ-integration to $(\pi/2,\pi)$. Then all integrations are elementary and yield:

$$-4\pi\ \vec{k}\cdot\hat{r}/\beta^3$$

Substitution of this result in (B.16) leads to:

$$M_3^s(k) = 2n\ \pi^{-\frac{1}{2}}(\beta m)^{-\frac{3}{2}}\int d\vec{r}\ g(r)(\vec{k}\cdot\hat{r})^2\delta(r-\sigma)$$

The remaining integrations over the space coordinates are also very easy and give finally:

$$M_3^s(k) = 8\pi^{\frac{1}{2}}ng(\sigma)(k\sigma)^2(\beta m)^{-\frac{3}{2}}/3 \qquad \text{(B.17)}$$

The third moment $M_3(k)$ of $F_k(t)$ follows from (B.4) as:

$$M_3(k) = M_3^s(k) + (N-1)\langle\exp(-i\vec{k}\cdot\vec{r}_1)(L_+)^3\exp(i\vec{k}\cdot\vec{r}_2)\rangle$$

In the same way as we arrived to (B.12) we get here by shifting one Liouville operator L_+ to the left:

$$M_3(k) = M_3^s(k) - (N-1)\langle(\vec{k}\cdot\vec{p}_1/m)\exp(-i\vec{k}\cdot\vec{r}_1)[\,L_o +$$

$$+\frac{1}{2}\sum_{i\neq j}\sum T_+(ij)](\vec{k}\cdot\vec{p}_2/m)\exp(i\vec{k}\cdot\vec{r}_2)\rangle$$

The free streaming part L_o gives a contribution:

$$-(N-1)\langle(\vec{k}\cdot\vec{p}_1/m)\exp(-i\vec{k}\cdot\vec{r}_1)\,i(\vec{k}\cdot\vec{p}_2/m)^2\exp(i\vec{k}\cdot\vec{r}_2)\rangle$$

This vanishes because of the factor $\vec{k}\cdot\vec{p}_1/m$. Thus the expression for $M_3(k)$ becomes:

$$M_3(k) = M_3^S(k) - (N-1)\langle(\vec{k}\cdot\vec{p}_1/m)\exp(-i\vec{k}\cdot\vec{r}_1)\frac{1}{2}\sum_{i\neq j}\sum T_+(ij)$$
$$(\vec{k}\cdot\vec{p}_2/m)\exp(i\vec{k}\cdot\vec{r}_2)\rangle$$

It is clear that the operator $T_+(ij)$ gives only a non vanishing contribution if the pair (ij) contains particle 2, so

$$M_3(k) = M_3^S(k) - (N-1)\langle(\vec{k}\cdot\vec{p}_1/m)\exp(-i\vec{k}\cdot\vec{r}_1)[T_+(12) +$$
$$+ \sum_{i=3}^{N} T_+(2i)](\vec{k}\cdot\vec{p}_2/m)\exp(i\vec{k}\cdot\vec{r}_2)\rangle \qquad (B.18)$$

Let us first consider a term with $T_+(2i)$, say

$$\langle(\vec{k}\cdot\vec{p}_1/m)\exp(-i\vec{k}\cdot\vec{r}_1)T_+(23)(\vec{k}\cdot\vec{p}_2/m)\exp(i\vec{k}\cdot\vec{r}_2)\rangle$$

This is zero because of the occurrence of $\vec{k}\cdot\vec{p}_1/m$. Thus from (B.18) there only results the term with $T_+(12)$:

$$M_3(k) = M_3^S(k) - (N-1)\langle(\vec{k}\cdot\vec{p}_1/m)\exp(-i\vec{k}\cdot\vec{r}_1)T_+(12)$$
$$(\vec{k}\cdot\vec{p}_2/m)\exp(i\vec{k}\cdot\vec{r}_2)\rangle$$

and again using (B. 14) this becomes:

$$M_3(k) = M_3^S(k) + (N-1)\langle(\vec{k}\cdot\vec{p}_1/m)(\vec{k}\cdot\hat{r}_{12})(\hat{r}_{12}\cdot\vec{p}_{12}/m)^2$$
$$\Theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)\exp(-i\vec{k}\cdot\vec{r}_{12})\rangle$$

After the introduction of the center of mass and the relative coordinates (B.15) we can calculate this average in precisely the same way as in the case of the self function. This leads to the following expression:

$$M_3(k) = (8/3)\,\pi^{\frac{1}{2}}\, ng(\sigma)\,(\beta m)^{-\frac{3}{2}}[\,(k\sigma)^2 - 3k\sigma\,\sin k\sigma - \qquad \text{(B.19)}$$

$$- 6\cos k\sigma + 6(\sin k\sigma)/k\sigma]$$

e) Velocity autocorrelation function

Finally we shall give some expressions for the first moments C_n of the velocity autocorrelation function $C_D(t)$. There is no need to calculate the coefficients C_n separately because they can be obtained from the moments of the self part of the intermediate scattering function $F_k^s(t)$ by means of the relation (1.35). By substituting for $F_k^s(t)$ its time expansion (1.37) and for $C_D(t)$ (1.38) one finds immediately for the moments C_n of $C_D(t)$:

$$C_n = -\beta m \lim_{k\to 0} M^s_{n+2}(k)/k^2 \qquad \text{(B.20)}$$

Inserting (B.10) and (B.17) in (B.20) one sees that the first moments are given by:

$$C_o = 1$$

$$C_1 = -(8/3)\,\pi^{\frac{1}{2}}\, n\sigma^2 g(\sigma)\,(\beta m)^{-\frac{1}{2}} \qquad \text{(B.21)}$$

APPENDIX C

THE MOMENTS OF THE TWO PARTICLE TERMS OF THE URSELL EXPANSION

The coefficient a_2 of t^2 in the Ursell expansion of $\varepsilon_k^{(2)}(t)$ follows from (2.24) and (2.35) as:

$$a_2 = \frac{1}{4} n^2 N^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12}) \{\exp(-i\vec{k}\cdot\vec{r}_1) + \exp(-i\vec{k}\cdot\vec{r}_2)\}[L^2(12) - L_o^2(12)]\{\exp(i\vec{k}\cdot\vec{r}_1) + \exp(i\vec{k}\cdot\vec{r}_2)\} \tag{C.1}$$

Noticing that, using (1.15) and (1.16):

$$L^2(12) - L_o^2(12) = L_I^2(12) + L_o(12)L_I(12) + L_I(12)L_o(12) \tag{C.2}$$

and that

$$L_I(12)\exp(i\vec{k}\cdot\vec{r}_1) = L_I(12)\exp(i\vec{k}\cdot\vec{r}_2) = 0$$

we find easily that:

$$[L^2(12) - L_o^2(12)]\{\exp(i\vec{k}\cdot\vec{r}_1) + \exp(i\vec{k}\cdot\vec{r}_2)\} = = -\frac{i\vec{k}}{m} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}\{\exp(i\vec{k}\cdot\vec{r}_1) - \exp(i\vec{k}\cdot\vec{r}_2)\} \tag{C.3}$$

Substituting this in (C.1) the expression for a_2 becomes:

$$a_2 = -\frac{1}{4} n^2 N^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12}) \{\exp(-i\vec{k}\cdot\vec{r}_1) + \exp(-i\vec{k}\cdot\vec{r}_2)\} \frac{i\vec{k}}{m} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \{\exp(i\vec{k}\cdot\vec{r}_1) - \exp(i\vec{k}\cdot\vec{r}_2)\}$$

which can also be written as:

$$a_2 = -\frac{1}{4}\, in^2 (Nm)^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12})$$

$$\{\exp(i\vec{k}\cdot\vec{r}_{12}) - \exp(-i\vec{k}\cdot\vec{r}_{12})\}\vec{k}\cdot\frac{\partial\varphi(r_{12})}{\partial\vec{r}_{12}}$$

After the introduction of the center of mass and relative coordinates $\vec{R}$ and $\vec{r}$ and after integration over $\vec{p}_1$, $\vec{p}_2$ and $\vec{R}$ we get:

$$a_2 = -\frac{1}{4}\, inm^{-1} \int d\vec{r}\; g(r)\{\exp(i\vec{k}\cdot\vec{r}) - \exp(-i\vec{k}\cdot\vec{r})\}\vec{k}\cdot\frac{\partial\varphi(r)}{\partial\vec{r}}$$

Now it is useful to average over the direction $\hat{k}$ of $\vec{k}$; this yields for a_2:

$$a_2 = \frac{1}{2}\, nkm^{-1} \int d\vec{r}\; g(r) j_1(kr)\hat{r}\cdot\frac{\partial\varphi(r)}{\partial\vec{r}}$$

with $j_1(kr)$ the first order spherical Bessel function (Abramowitz, Stegun, 1965). The integrations over the angles $\hat{r}$ can be carried out, resulting in:

$$a_2 = 2\pi nkm^{-1} \int_0^\infty r^2 g(r) j_1(kr)\varphi'(r)\,dr \qquad \text{(C.4)}$$

The intermediate scattering function $F_k(t)$ follows from (1.32) as:

$$F_k(t) = S(k)\;\{\exp(-k^2t^2/2\beta m) + \varepsilon_k(t)\} \qquad \text{(C.5)}$$

Expanding the exponentional in a power series in t and substituting the series for $\varepsilon_k(t)$ we find:

$$F_k(t) = S(k)\{1 - k^2t^2/2\beta m + a_2 t^2 + 0(t^4)\} \qquad \text{(C.6)}$$

With (1.37) the moments of the Ursell expansion can be obtained from this expression as:

$$M_o^u = S(k)$$
$$M_2^u = S(k)(-k^2/\beta m+2a_2) \qquad (C.7)$$

with a_2 given by (C.4).

The two particle term of the self part of the intermediate scattering function follows from (2.11) and (2.13) as:

$$\varepsilon_k^{s(2)}(t) = n^2N^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1)U_t(12)\exp(i\vec{k}\cdot\vec{r}_1) \qquad (C.8)$$

To calculate the coefficients of the successive powers of t again the expansion (2.35) will be used. After substituting this expression in (C.8) one sees immediately that the coefficients of the zeroth and first power of t are zero. The coefficient a_2^s of t^2 follows as:

$$a_2^s = \frac{1}{2}n^2N^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\exp(-i\vec{k}\cdot\vec{r}_1) \{L^2(12)-L_o^2(12)\}\exp(i\vec{k}\cdot\vec{r}_1)$$

Using (C.2) and (C.3) a_2^s becomes:

$$a_2^s = -\frac{1}{2}in^2(Nm)^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\vec{k}\cdot\frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}$$

Because of isotropy this may be averaged over the direction $\hat{k}$ of $\vec{k}$, resulting in:

$$a_2^s = 0 \qquad (C.9)$$

The coefficient a_3^s of t^3 follows from (C.8) and (2.35) as:

$$a_3^s = \frac{1}{6} n^2 N^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$\{L^3(12) - L_o^3(12)\} \exp(i\vec{k}\cdot\vec{r}_1)$$

After working out the effect of the Liouville operators on $\exp(i\vec{k}\cdot\vec{r}_1)$ the expression becomes:

$$a_3^s = \frac{1}{6} n^2 N^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12})$$

$$\{-3(i\vec{k}\cdot\vec{p}_1/m) \frac{i\vec{k}}{m} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} - \frac{(\vec{p}_1-\vec{p}_2)}{m} \cdot \frac{\partial}{\partial\vec{r}_1} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{i\vec{k}}{m}\}$$

The integrations over the momenta $\vec{p}_1$ and $\vec{p}_2$ are easy and lead again to a result zero:

$$a_3^s = 0 \qquad \text{(C.10)}$$

From (C.8) and (2.35) the coefficient a_4^s of t^4 can be derived as:

$$a_4^s = n^2 (24N)^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12})$$

$$\exp(-i\vec{k}\cdot\vec{r}_1)\{L^4(12) - L_o^4(12)\} \exp(i\vec{k}\cdot\vec{r}_1)$$

which, after calculation of the effect of the operators, leads to:

$$a_4^s = \frac{1}{24} n^2 N^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12})$$

$$[-4(i\vec{k}\cdot\vec{p}_1/m)\{\frac{(\vec{p}_1-\vec{p}_2)}{m} \cdot \frac{\partial}{\partial\vec{r}_1} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{i\vec{k}}{m}\}$$

$$-6(i\vec{k}\cdot\vec{p}_1/m)^2\{\frac{i\vec{k}}{m} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}\} + 3\{\frac{i\vec{k}}{m} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}\}^2$$

$$-(\frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial\vec{r}_1})\{\frac{(\vec{p}_1-\vec{p}_2)}{m} \cdot \frac{\partial}{\partial\vec{r}_1}\} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{i\vec{k}}{m}$$

$$+(\frac{\vec{p}_2}{m} \cdot \frac{\partial}{\partial\vec{r}_1})\{\frac{(\vec{p}_1-\vec{p}_2)}{m} \cdot \frac{\partial}{\partial\vec{r}_1}\} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{i\vec{k}}{m}$$

$$+ \frac{2}{m} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{\partial}{\partial\vec{r}_1} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{i\vec{k}}{m}]$$

Averaging over $\hat{k}$ simplifies this expression considerably, because all terms, that contain an uneven power of $\vec{k}$, disappear:

$$a_4^s = \frac{1}{24} n^2 k^2 N^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12})$$

$$\{\frac{4}{3m} \frac{(\vec{p}_1-\vec{p}_2)}{m} \cdot \frac{\partial}{\partial\vec{r}_1} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{\vec{p}_1}{m} - \frac{1}{m^2} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}\}$$

After integration over the momenta $\vec{p}_1$ and $\vec{p}_2$ this coefficient becomes:

$$a_4^s = \frac{1}{24} n^2 k^2 (Nm^2)^{-1} \int d\vec{r}_1 d\vec{r}_2 g(r_{12}) \{\frac{4}{3\beta} \frac{\partial}{\partial\vec{r}_1} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} - \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}\} \qquad (C.\ 11)$$

Finally the introduction of center of mass and relative coordinates $\vec{R}$ resp. $\vec{r}$ yields:

$$a_4^s = \frac{1}{24} nk^2 m^{-2} \int d\vec{r} g(r) \{\frac{4}{3} \beta^{-1} \vec{\nabla}^2 \varphi(r) - (d\varphi/dr)^2\} \qquad (C.12)$$

Using (1.32), (C.9), (C.10) and (C.12) one finds for the time expansion of $F_k^s(t)$:

$$F_k^s(t) = \exp(-k^2 t^2/2\beta m) + \varepsilon_k^s(t)$$

$$= 1 - k^2 t^2/2\beta m + \frac{1}{8} k^4 t^4 (\beta m)^{-2} + a_4^s t^4 + 0(t^6)$$

So with (1.37) the moments follow as:

$$M_o^{s,u} = 1$$

$$M_2^{s,u} = -k^2/\beta m \qquad (C.13)$$

$$M_4^{s,u} = 3k^4 (\beta m)^{-2} + 24 a_4^s$$

with a_4^s given by (C.12).

It should be noted that (C.11) can be written in another form by using the static relation between the pair correlation function and the triple distribution function (Münster, 1969):

$$\frac{\partial g(r_{12})}{\partial \vec{r}_1} = -\beta \frac{\partial \varphi(r_{12})}{\partial \vec{r}_1} g(r_{12}) - n\beta \int d\vec{r}_3 \frac{\partial \varphi(r_{13})}{\partial \vec{r}_1} g(\vec{r}_1\vec{r}_2\vec{r}_3) \tag{C.14}$$

Replacing of one vector $\partial\varphi(r_{12})/\partial\vec{r}_1$ by means of this relation in the last term of (C.11) yields for a_4^s:

$$a_4^s = \frac{1}{24} n^2 k^2 (Nm^2\beta)^{-1} \int d\vec{r}_1 d\vec{r}_2 \{\frac{4}{3} g(r_{12}) \frac{\partial}{\partial \vec{r}_1} \cdot \frac{\partial \varphi(r_{12})}{\partial \vec{r}_1}$$
$$+ \frac{\partial \varphi(r_{12})}{\partial \vec{r}_1} \cdot \frac{\partial g(r_{12})}{\partial \vec{r}_1} + \frac{\partial \varphi(r_{12})}{\partial \vec{r}_1} \cdot n \int d\vec{r}_3 \frac{\partial \varphi(r_{13})}{\partial \vec{r}_1} g(r_1 r_2 r_3)\}$$

The second term may be reduced by partial integration:

$$\int d\vec{r}_1 d\vec{r}_2 \frac{\partial \varphi(r_{12})}{\partial \vec{r}_1} \cdot \frac{\partial g(r_{12})}{\partial \vec{r}_1} = -\int d\vec{r}_1 d\vec{r}_2 g(r_{12}) \frac{\partial}{\partial \vec{r}_1} \cdot \frac{\partial \varphi(r_{12})}{\partial \vec{r}_1}$$

In the terms containing the pair correlation function $g(r_{12})$ now center of mass and relative coordinates, $\vec{R}$ and $\vec{r}$, are introduced, leading finally to:

$$a_4^s = \frac{1}{72} nk^2 (m^2\beta)^{-1} \int d\vec{r}\, g(r) \vec{\nabla}^2 \varphi(r)$$
$$+ \frac{1}{24} n^3 k^2 (Nm^2\beta)^{-1} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 g(\vec{r}_1\vec{r}_2\vec{r}_3) \frac{\partial \varphi(r_{12})}{\partial \vec{r}_1} \cdot \frac{\partial \varphi(r_{13})}{\partial \vec{r}_1} \tag{C.15}$$

where the first term gives the exact fourth moment (1.40).

The two particle term of the velocity autocorrelation function was derived in (2.33):

$$C_D^{(2)}(t) = \frac{1}{3} \beta n^2 (Nm)^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12}) \vec{p}_1 \cdot U_t(12) \vec{p}_1 \tag{C.16}$$

After substituting (2.35) one sees immediately that the constant, a_o^c, vanishes. The coefficient a_1^c of t is:

$$a_1^c = \frac{1}{3}\beta n^2 (Nm)^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12})\vec{p}_1 \cdot L_I(12)\vec{p}_1$$

$$= -\frac{1}{3}\beta n^2 (Nm)^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12})\vec{p}_1 \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}$$

Integration over $\vec{p}_1$ leads to a result zero:

$$a_1^c = 0 \qquad \text{(C.17)}$$

The coefficient a_2^c of t^2 follows from (C.16) and (2.35) as:

$$a_2^c = \frac{1}{6}\beta n^2 (Nm)^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12})\vec{p}_1 \cdot$$

$$\cdot\, [L^2(12) - L_o^2(12)]\vec{p}_1$$

$$= -\frac{1}{6}\beta n^2 (Nm)^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12})$$

$$\frac{(\vec{p}_1 - \vec{p}_2)}{m} \cdot \frac{\partial}{\partial\vec{r}_1}\frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \vec{p}_1$$

The integrations over the momenta $\vec{p}_1$ and $\vec{p}_2$ and the center of mass coordinates $\vec{R}$ are elementary and yield finally:

$$a_2^c = -\frac{n}{6m}\int d\vec{r}\; g(r)\vec{\nabla}^2\varphi(r) \qquad \text{(C.18)}$$

From (2.22), (C.17) and (C.18) it follows that:

$$C_D(t) = 1 + a_2^c t^2 + 0(t^4)$$

Comparison with (1.38) gives the moments:

$$
\begin{aligned}
C_o^u &= 1 \\
C_2^u &= 2a_2^c = -\frac{1}{3}\, nm^{-1} \int d\vec{r}\; g(r)\vec{\nabla}^2\varphi(r)
\end{aligned}
\qquad (C.19)
$$

what is the exact value (1.41).

APPENDIX D

THE MOMENTS OF THE TWO PARTICLE TERMS OF THE SECOND DERIVATIVE EXPANSION

The two particle term $F_k^{(2)}(t)$ of the intermediate scattering function $F_k(t)$ follows from (2.53) as:

$$F_k^{(2)}(t) = in^2N^{-1}\int_o^t dt'\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\vec{k}\cdot\vec{p}_1/m$$

$$\exp(-i\vec{k}\cdot\vec{r}_1)U_{t'}(12)[\exp(i\vec{k}\cdot\vec{r}_1)+\exp(i\vec{k}\cdot\vec{r}_2)] \quad \text{(D.1)}$$

We shall write this as a power series in t:

$$F_k^{(2)}(t) = a_1t+a_2t^2+a_3t^3+a_4t^4+\ldots \quad \text{(D.2)}$$

by means of (2.35). Substituting (2.35) in (D.1) one sees immediately that

$$a_1 = a_2 = 0 \quad \text{(D.3)}$$

For a_3 we find:

$$a_3 = \frac{1}{6}\, in^2N^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\vec{k}\cdot\vec{p}_1/m \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$[L^2(12)-L_o^2(12)][\exp(i\vec{k}\cdot\vec{r}_1)+\exp(i\vec{k}\cdot\vec{r}_2)]$$

After working out the Liouville operators this becomes:

$$a_3 = \frac{1}{6}\, n^2N^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\vec{k}\cdot\vec{p}_1/m \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$\frac{\vec{k}}{m}\cdot\frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}[\exp(i\vec{k}\cdot\vec{r}_1)-\exp(i\vec{k}\cdot\vec{r}_2)]$$

Because of the occurrence of $\vec{k}\cdot\vec{p}_1/m$ in this expression the integration over $\vec{p}_1$ gives zero:

$$a_3 = 0 \tag{D.4}$$

The coefficient a_4 is found to be:

$$a_4 = in^2(24N)^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12}) \vec{k}\cdot\vec{p}_1/m \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$[L^3(12)-L_o^3(12)][\exp(i\vec{k}\cdot\vec{r}_1)+\exp(i\vec{k}\cdot\vec{r}_2)]$$

and after some calculations this becomes:

$$a_4 = -in^2(24N)^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2) g(r_{12}) \vec{k}\cdot\vec{p}_1/m$$

$$\exp(-i\vec{k}\cdot\vec{r}_1)[(\frac{(\vec{p}_1-\vec{p}_2)}{m} \cdot \frac{\partial}{\partial\vec{r}_1} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{i\vec{k}}{m})(\exp(i\vec{k}\cdot\vec{r}_1)-$$

$$-\exp(i\vec{k}\cdot\vec{r}_2)) + 3\,\frac{i\vec{k}}{m} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}(i\vec{k}\cdot\vec{p}_1/m \exp(i\vec{k}\cdot\vec{r}_1)-$$

$$-i\vec{k}\cdot\vec{p}_2/m \exp(i\vec{k}\cdot\vec{r}_2))]$$

The integrations over the momenta are simple, resulting in:

$$a_4 = -in^2 m(24N\beta)^{-1}\int d\vec{r}_1 d\vec{r}_2 g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$[m^{-2}(k \cdot \frac{\partial}{\partial\vec{r}_1} \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1} \cdot \frac{i\vec{k}}{m})(\exp(i\vec{k}\cdot\vec{r}_1)-\exp(i\vec{k}\cdot\vec{r}_2))$$

$$+3ik^2m^{-2}(\frac{i\vec{k}}{m} \cdot \frac{\partial\varphi(r_{12})}{\partial\vec{r}_1}) \exp(i\vec{k}\cdot\vec{r}_1)]$$

After the introduction of the center of mass and relative coordinates, $\vec{R}$ and $\vec{r}$ (2.25), the integration over $\vec{R}$ can be performed. The last term in the integrand gives a result zero because of isotropy. Then the coefficient a_4 becomes:

$$\begin{aligned} a_4 &= n(24m^2\beta)^{-1}\int d\vec{r} g(r)(1-\exp(-i\vec{k}\cdot\vec{r}))(\vec{k}\cdot\vec{\nabla})^2\varphi(r) \\ &= n(24m^2\beta)^{-1}\int d\vec{r} g(r)(1-\cos \vec{k}\cdot\vec{r})(k\cdot\vec{\nabla})^2\varphi(r) \end{aligned} \tag{D.5}$$

The time expansion of the intermediate scattering function $F_k(t)$ follows then from (2.49) and (D.2)-(D.5) as:

$$F_k(t) = S(k)-1+\exp(-k^2t^2/2\beta m)+F_k^{(2)}(t)$$
$$= S(k)-k^2t^2/2\beta m+(\frac{1}{8}k^4(\beta m)^{-2}+a_4)t^4+O(t^6) \qquad (D.6)$$

Comparison of (D.6) with (1.37) shows for the moments of the second derivative expansion:

$$M_o^{(2)}(k) = S(k)$$
$$M_2^{(2)}(k) = -k^2/\beta m \qquad (D.7)$$
$$M_4^{(2)}(k) = 3k^4(\beta m)^{-2}+24a_4$$

They all agree with the exact values.

The two particle term $F_k^{s(2)}(t)$ of the self function is given by:

$$F_k^{s(2)}(t) = in^2N^{-1}\int_o^t dt'\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})$$
$$\vec{k}\cdot\vec{p}_1/m \exp(-i\vec{k}\cdot\vec{r}_1)U_{t'}(12)\exp(i\vec{k}\cdot\vec{r}_1)$$

We write this as the following power series in t:

$$F_k^{s(2)}(t) = a_1^s t+a_2^s t^2+a_3^s t^3+a_4^s t^4+\ldots \qquad (D.8)$$

The calculation of these coefficients is carried out in exactly the same way as $a_1\ldots a_4$. The results are:

$$a_1^s = a_2^s = a_3^s = 0$$
$$a_4^s = n(24m^2\beta)^{-1}\int d\vec{r}\ g(r)(\vec{k}\cdot\vec{\nabla})^2\varphi(r) \qquad (D.9)$$

Because of isotropy a_4^s can also be written as:

$$a_4^s = nk^2(72m^2\beta)^{-1}\int d\vec{r}\ g(r)\vec{\nabla}^2\varphi(r) \tag{D.10}$$

The time expansion of $F_k^s(t)$ follows then from (2.49) and (D.8)-(D.10) as:

$$F_k^s(t) = 1-k^2t^2/2\beta m+(\frac{1}{8}\ k^4(\beta m)^{-2}+a_4^s)t^4+0(t^6)$$

and with (1.37) there results for the moments:

$$M_o^{s(2)}(k) = 1$$

$$M_2^{s(2)}(k) = -k^2/\beta m \tag{D.11}$$

$$M_4^{s(2)}(k) = 3k^4(\beta m)^{-2}+24a_4^s$$

They also agree with the exact values.

APPENDIX E

DETAILED CALCULATION OF THE DEVIATIONS FROM THE IDEAL GAS BEHAVIOUR FOR THE HARD SPHERES SYSTEM

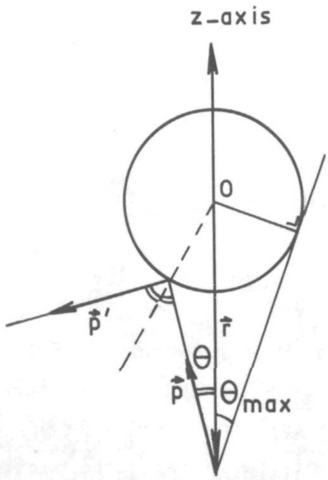
In (2.31) we found for the deviation of the coherent intermediate scattering function from its ideal gas value:

$$\varepsilon_k^{(2)}(t) = n\ \exp(-k^2t^2/4\beta m)\int d\vec{p}d\vec{r}\varphi(p)\sigma(r)[\ j_o(k|\vec{r}+\vec{r}(t)|/2)$$

$$+j_o(k|\vec{r}-\vec{r}(t)|/2)-j_o(kpt/m)-j_o(k|\vec{r}+\vec{p}t/m|)] \qquad (E.1)$$

The trajectory $\vec{r}(t)$ for hard spheres has been given in (3.8) while the collision time τ follows from (3.9). The function between the square brackets on the right hand side of (E.1) depends only on the magnitude of the initial interparticle distance r, the magnitude of the initial relative momentum p and on the angle between $\vec{r}$ and $\vec{p}$; this function will in the following be denoted by $h_k(p,r,\hat{p}\cdot\hat{r};t)$ where $\hat{p}$ and $\hat{r}$ are the directions of resp. $\vec{p}$ and $\vec{r}$.

It is easy to see that $h_k = 0$ as long as $t < \tau$. This means that the particle must have a momentum larger than some minimum momentum p_{min} to reach the sphere within the time t. To determine the boundaries of the integrations that are contained in (E.1) we take first the initial relative position $\vec{r}$ fixed along the negative z-axis (see fig. 25). In spherical coordinates the components of $\vec{p}$ are: its magnitude p, the angle θ_p between $\vec{p}$ and the z-axis and some polar angle φ_p, where p runs from p_{min} to ∞, θ_p from 0 to a maximum value θ_{max} and φ_p from 0 to 2π. θ_{max} is given by (see fig. 25): $\sin\theta_{max} = \sigma/r$ so $\theta_{max} = \arcsin\sigma/r$. The integration over φ_p can immediately be carried out and gives a factor 2π. For $\vec{r}$ one can write $r\hat{r}$ where $\hat{r}$ is the direction of $\vec{r}$. Because of spherical symmetry the integration over $\hat{r}$ contributes a factor 4π. The range of r runs from σ to ∞. Now (E.1) becomes with $\hat{p}\cdot\hat{r} = -\cos\theta_p$:



$$\vec{r}(t)=\vec{r}+2\vec{p}t/m \qquad t \le \tau$$

$$=\vec{r}+2\vec{p}\tau/m+2\vec{p}\,'(t-\tau)/m \qquad t > \tau$$

$$\vec{p}(t)=\vec{p} \qquad t \le \tau$$

$$=\vec{p}\,' \qquad t > \tau$$

$$\vec{\sigma}=\vec{r}+2\vec{p}\tau/m$$

$$\vec{p}\,' =\vec{p}-2(\vec{p}\cdot\hat{\sigma})\hat{\sigma}$$

Fig. 25. The hard spheres binary collision. The meaning of the symbols is explained in the text.

$$\varepsilon_k^{(2)}(t) = 8\pi^2 n \exp(-k^2t^2/4\beta m)\int_\sigma^\infty r^2 g(r)\,dr\int_o^{\theta_{max}} \sin\theta_p d\theta_p \int_{p_{min}}^\infty p^2\varphi(p)\,dp\; h_k(p,r,\cos\theta_p;t)$$

Introducing for θ_p a new variable $u = \cos\theta_p$ one gets:

$$\varepsilon_k^{(2)}(t) = 8\pi^2 n \exp(-k^2t^2/4\beta m)\int_\sigma^\infty r^2 g(r)\,dr \int_{(1-\sigma^2/r^2)^{1/2}}^{1} du \int_{p_{min}}^\infty p^2\varphi(p)\,dp\; h_k(p,r,u;t) \qquad (E.2)$$

We shall now introduce reduced variables. The distance r can be made dimensionless by the sphere diameter σ, so we write $r = \sigma\rho$ where ρ is the dimensionless interparticle distance. The momentum p can be reduced by the mean momentum p_o in some direction, say with $p_o = (m/\beta)^{1/2}$, so the dimensionless momentum w follows from $p = p_o w$. Furthermore one can introduce a dimensionless time $t^* = p_o t/(\sigma m)$. One sees that t^* is the ratio of the observation time t and the time that a particle with thermal velocity p_o/m needs to travel a distance σ. Finally we introduce a reduced density $n^* = n\sigma^3$ and a reduced wave vector $k^* = k\sigma$.

Substitution of these new variables in (E.2) leads to the following expression:

$$\varepsilon_k^{(2)}(t) = 8n^*\pi^{1/2}\exp(-k^{*2}t^{*2}/4)\int_1^\infty \rho^2 g(\rho)\,d\rho \int_{(1-1/\rho^2)^{1/2}}^{1} du \int_{w_{min}}^{\infty} w^2 e^{-w^2} h_k(\rho,w,u;t^*)\,dw \tag{E.3}$$

where use has been made of (2.26).

Equation (3.9) for the collision time τ has in the new reduced variables the solution:

$$\tau^* = [\rho u-(\rho^2u^2-\rho^2+1)^{1/2}]/2w \tag{E.4}$$

We now introduce for the angle u a new variable v that is proportional to the collision time τ^*:

$$v = \rho u-(\rho^2u^2-\rho^2+1)^{1/2}$$

Then the collision time becomes very simple:

$$\tau^* = v/2w$$

The condition $t > \tau$ must be fulfilled, so $t^* > \tau^* = v/2w$ and we find for the minimum momentum $w_{min} = v/2t^*$. So one gets finally for the deviation $\varepsilon_k^{(2)}(t)$:

$$\varepsilon_k^{(2)}(t) = 8n^*\pi^{1/2}\exp(-k^{*2}t^{*2}/4)\int_1^\infty \rho\, g(\rho)\,d\rho \int_{\rho-1}^{(\rho^2-1)^{1/2}} -(v^2-\rho^2+1)/(2v^2)\,dv \int_{v/2\,t^*}^\infty dw\, w^2\exp(-w^2)\,h_k(w,\rho,v;t^*) \quad (E.5)$$

where

$$h_k(w,\rho,v;t^*) = j_o(a_1)+j_o(a_2)-j_o(a_3)-j_o(a_4)$$

$$a_1 = \frac{1}{2}k^*[-(\rho^2-v^2-1)^2+4v^2+4+2wt^*\{(\rho^2-v^2)^2-4v^2-1\}/v+4w^2t^{*2}]^{1/2}$$

$$a_2 = \frac{1}{2}k^*[(1-2wt^*/v)(v^2-\rho^2+1)^2+4w^2t^{*2}]^{1/2} \quad (E.6)$$

$$a_3 = k^*t^*w$$

$$a_4 = k^*[\rho^2-wt^*(v^2+\rho^2-1)/v+w^2t^{*2}]^{1/2}$$

The deviation $\varepsilon_k^{s(2)}(t)$ of the incoherent intermediate scattering function follows from (2.32) in completely the same way as:

$$\varepsilon_k^{s(2)}(t) = 8n^*\pi^{1/2}\exp(-k^{*2}t^{*2}/4)\int_1^\infty \rho\, g(\rho)\,d\rho \int_{\rho-1}^{(\rho^2-1)^{1/2}} -(v^2-\rho^2+1)/(2v^2)\,dv \int_{v/2\,t^*}^\infty dw\, w^2\exp(-w^2)\,h_k^s(w,\rho,v;t^*) \quad (E.7)$$

with

$$h_k^s(\rho,w,v;t^*) = j_o(a_2)-j_o(a_3)$$

where a_2 and a_3 are given in (E.6).

The deviation of the velocity autocorrelation function can be handled analogously. Taking as starting point expression (2.34) for $C_D^{(2)}(t)$ we find after substitution of (3.7) and (3.9):

$$C_D^{(2)}(t) = -\frac{2}{3} n\pi^{-3/2} (\beta/m)^{5/2} \sigma^{-2} \int d\vec{p} d\vec{r} \exp(-\beta p^2/m)$$
$$g(r) (\vec{p}\cdot\vec{r}+2p^2\tau/m)^2 \theta(t-\tau) \qquad \text{(E.8)}$$

where use has been made of (2.26). We can now go on in the same way as in the case of the intermediate scattering functions and introduce the reduced variables ρ, v and w. Comparing (E.8) with the corresponding deviation (E.1) of the intermediate scattering function one observes that the integrand of (E.8) has a far more simple structure. This has as a consequence that in this case the v- and w-integrations can be done, resulting in:

$$C_D^{(2)}(t) = \frac{2}{3} \pi^{1/2} n^* \int_1^\infty \rho\, g(\rho) I(\rho;t^*) d\rho \qquad \text{(E.9)}$$

where $I(\rho;t^*)$ is given by:

$$I(\rho;t^*) = [-(\rho-1)/t^* - 4t^*(\rho-1)(\rho+2) + 8t^{*3}] \exp(-(\rho-1)^2/4t^{*2})$$
$$+[-1+3(\rho-1)+6(\rho-1)^2+2(\rho-1)^3] \pi^{1/2} \mathrm{erfc}((\rho-1)/2t^*)$$
$$+[-8t^{*3}+4t^*(\rho^2-1)] \exp(-(\rho^2-1)/4t^{*2})$$
$$-2\pi^{1/2}(\rho^2-1)^{3/2} \mathrm{erfc}((\rho^2-1)^{1/2}/2t^*) \qquad \text{(E.10)}$$

with erfc(z) the complementary error function, defined by (Abramowitz, Stegun, 1965):

$$\mathrm{erfc}(z) = 2\pi^{-1/2} \int_z^\infty \exp(-t^2) dt \qquad \text{(E.11)}$$

Fig. 26 shows the function $I(\rho;t^*)$.

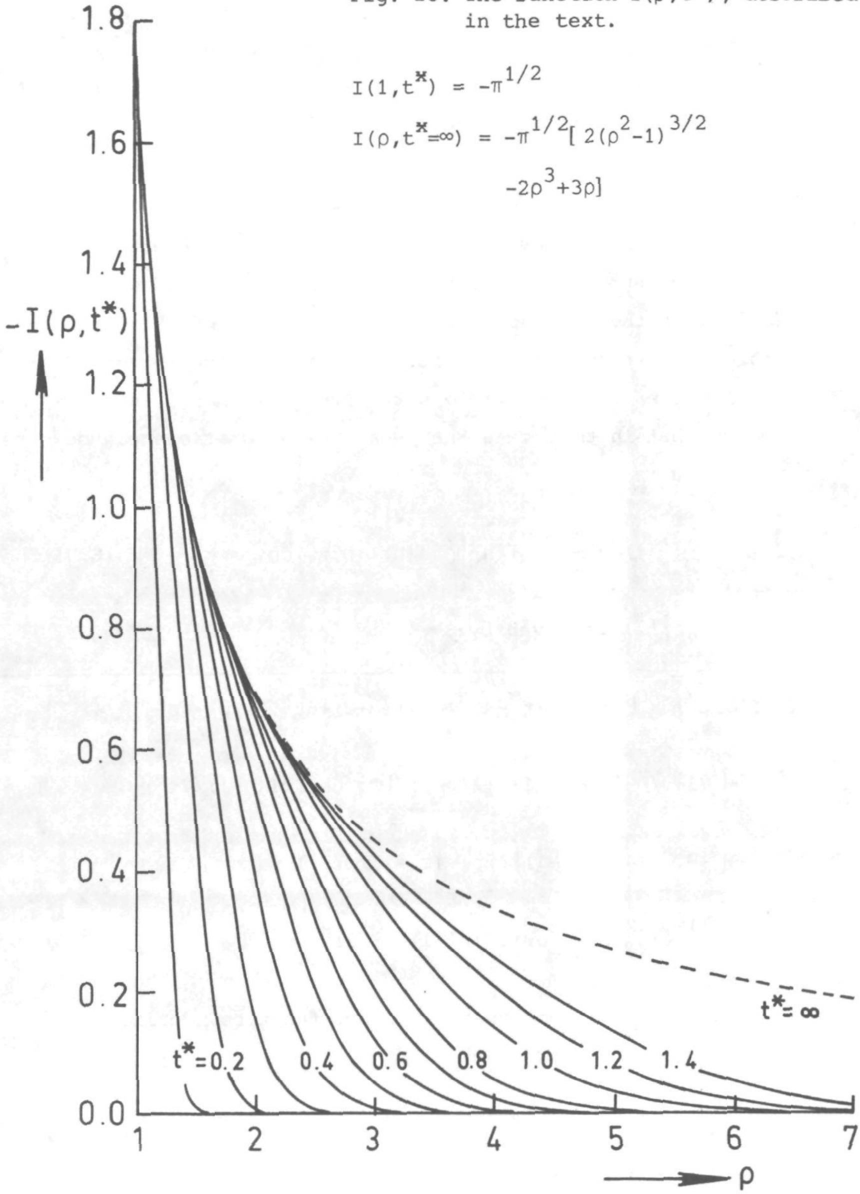


Fig. 26. The function $I(\rho,t^*)$, described in the text.

$$I(1,t^*) = -\pi^{1/2}$$

$$I(\rho,t^*{=}\infty) = -\pi^{1/2}[\,2(\rho^2-1)^{3/2} -2\rho^3+3\rho]$$

APPENDIX F

THE MOMENTS OF THE HARD SPHERES URSELL EXPANSION

In chapter 2 detailed expressions for the deviations of the correlation functions from the ideal gas behaviour were derived. From (2.11) and (2.23) the deviation $\varepsilon_k^{(2)}(t)$ of the intermediate scattering function follows as:

$$\varepsilon_k^{(2)}(t) = n^2 N^{-1}\int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1) U_t(12) \sum_{j=1}^{2} \exp(i\vec{k}\cdot\vec{r}_j) \tag{F.1}$$

The term with j=1 gives the self part $\varepsilon_k^{s(2)}(t)$. Writing the deviations as an expansion in powers of t:

$$\varepsilon_k^{(2)}(t) = \sum_{n=0}^{\infty} a_n t^n$$

and (F.2)

$$\varepsilon_k^{s(2)}(t) = \sum_{n=0}^{\infty} a_n^s t^n$$

the coefficients a_n and a_n^s follow after substitution from (2.35) in (F.1) as:

$$a_m = n^2 (Nm!)^{-1}\int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1) [L^m(12) - L_o^m(12)] \sum_{j=1}^{2} \exp(i\vec{k}\cdot\vec{r}_j) \tag{F.3}$$

The term with j=1 gives again a_m^s. One sees immediately that

$$a_o = a_o^s = 0 \tag{F.4}$$

and because $[L(12) - L_o(12)]\exp(i\vec{k}\cdot\vec{r}_j) = T_+(12)\exp(i\vec{k}\cdot\vec{r}_j) = 0$ that

$$a_1 = a_1^s = 0 \tag{F.5}$$

The coefficient a_2 follows from (F.3) as:

$$a_2 = \frac{1}{2} n^2 N^{-1} \int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$[L^2(12) - L_o^2(12)] \sum_{j=1}^{2} \exp(i\vec{k}\cdot\vec{r}_j)$$

The operator between square brackets can be written as:

$$L^2 - L_o^2 = (L_o + T_+)^2 - L_o^2 = L_o T_+ + T_+ L_o + T_+^2$$

So we see that only $T_+ L_o$ gives a contribution to a_2. After working out the effect of $T_+ L_o$ on $\Sigma \exp(i\vec{k}\cdot\vec{r}_j)$, using (1.22), we arrive at:

$$a_2 = \frac{1}{2} in^2 N^{-1} \int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$\{\exp(i\vec{k}\cdot\vec{r}_1) - \exp(i\vec{k}\cdot\vec{r}_2)\}(\vec{p}_{12}\cdot\hat{r}_{12}/m)^2$$

$$(\vec{k}\cdot\hat{r}_{12})\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)$$

The coefficient a_2^s is found by taking only the term $\exp(i\vec{k}\cdot\vec{r}_1)$.

Introduction of center of mass and relative coordinates, $\vec{P}$, $\vec{R}$ resp. $\vec{p}$, $\vec{r}$, followed by an integration over $\vec{P}$ and $\vec{R}$ yields for a_2:

$$a_2 = \frac{1}{2} in \int d\vec{r} d\vec{p} \varphi(p) g(r) \{1 - \exp(-i\vec{k}\cdot\vec{r})\}(\hat{r}\cdot 2\vec{p}/m)^2$$

$$(\vec{k}\cdot\hat{r})\theta(-\vec{p}\cdot\vec{r})\delta(r-\sigma) \tag{F.6}$$

The term with 1 between the curly brackets gives a_2^s; one sees immediately that

$$a_2^s = 0 \tag{F.7}$$

The remaining integrations in (F.6) are elementary; using (2.26) we find finally for a_2:

$$a_2 = -2\pi n(\beta m)^{-1} k\sigma^2 g(\sigma) j_1(k\sigma) \tag{F.8}$$

with $j_1(k\sigma)$ the first order spherical Bessel function (2.36).

The coefficient a_3 follows from (F.3) as:

$$a_3 = \frac{1}{6} n^2 N^{-1} \int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$\{L^3(12) - L_o^3(12)\} \sum_{j=1}^{2} \exp(i\vec{k}\cdot\vec{r}_j)$$

and because $T_+(12)$, working on a function of the coordinates only, gives no contribution this amounts to:

$$a_3 = \frac{1}{6} n^2 N^{-1} \int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$\{L_o(12)T_+(12) + T_+(12)L_o(12) + T_+^2(12)\} L_o(12) \sum_{j=1}^{2} \exp(i\vec{k}\cdot\vec{r}_j) \tag{F.9}$$

The term with j=1 gives the coefficient a_3^s of the self part $\varepsilon_k^{s(2)}(t)$.

The operator $T_+^2(12)$ does not contribute to a_3 because two spheres cannot collide twice with each other. The term with T_+L_o can be written as:

$$-\frac{1}{6} n^2 N^{-1} \int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_1)$$

$$T_+(12) \sum_{j=1}^{2} (\vec{k}\cdot\vec{p}_j/m)^2 \exp(i\vec{k}\cdot\vec{r}_j)$$

The effect of $T_+(12)$ on the term with j=1 is:

$$\frac{1}{6}n^2(Nm^3)^{-1}\int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2)g(r_{12})(\vec{p}_{12}\cdot\hat{r}_{12})\theta(-\vec{p}_{12}\cdot\vec{r}_{12})$$

$$\delta(r_{12}-\sigma)\{(\vec{p}_{12}\cdot\hat{r}_{12})^2(\vec{k}\cdot\hat{r}_{12})^2-2(\vec{k}\cdot\vec{p}_1)(\vec{k}\cdot\hat{r}_{12})(\vec{p}_{12}\cdot\hat{r}_{12})\}$$

After interchanging particles 1 and 2 and adding both expressions, this becomes:

$$-\frac{1}{6}n^2(Nm^3)^{-1}\int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2)g(r_{12})(\vec{p}_{12}\cdot\hat{r}_{12})^2(\vec{k}\cdot\hat{r}_{12})$$

$$\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)[\vec{k}\cdot(\vec{p}_{12}-(\vec{p}_{12}\cdot\hat{r}_{12})\hat{r}_{12})]$$

Observing that $\vec{p}_{12}-(\vec{p}_{12}\cdot\hat{r}_{12})\hat{r}_{12}$ is the component of $\vec{p}_{12}$ perpendicular to $\hat{r}_{12}$, one sees immediately that this term, after integration over the angle of $\vec{p}_{12}$ with respect to $\hat{r}_{12}$, vanishes. In the same way the term with $j=2$ can be shown to be 0.

Thus in (F.9) only the operator $L_o T_+$ gives a finite contribution to a_3:

$$a_3 = \frac{1}{6}\, in^2 N^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\exp(-i\vec{k}\cdot\vec{r}_1)$$

$$L_o(12)T_+(12)\sum_{j=1}^{2}(\vec{k}\cdot\vec{p}_j/m)\exp(i\vec{k}\cdot\vec{r}_j)$$

$$= \frac{1}{6}\, in^2 N^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\exp(-i\vec{k}\cdot\vec{r}_1)$$

$$L_o(12)[\exp(i\vec{k}\cdot\vec{r}_1)-\exp(i\vec{k}\cdot\vec{r}_2)](\vec{p}_{12}\cdot\hat{r}_{12}/m)^2(\vec{k}\cdot\hat{r}_{12})$$

$$\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)$$

After partial integration with respect to $\vec{r}_1$ and $\vec{r}_2$ this becomes:

$$a_3 = -\frac{1}{6}\, in^2 N^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)[\, L_o(12) g(r_{12})$$

$$\exp(-i\vec{k}\cdot\vec{r}_1)][\exp(i\vec{k}\cdot\vec{r}_1)-\exp(i\vec{k}\cdot\vec{r}_2)]\,(\vec{p}_{12}\cdot\hat{r}_{12}/m)^2 (\vec{k}\cdot\hat{r}_{12})$$

$$\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)$$

$$= -\frac{1}{6}\, in^2 (Nm^3)^{-1} \int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)[\vec{p}_{12}\cdot\hat{r}_{12} g'(r_{12})-$$

$$-i\vec{k}\cdot\vec{p}_1 g(r_{12})][1-\exp(-i\vec{k}\cdot\vec{r}_{12})]\,(\vec{p}_{12}\cdot\hat{r}_{12})^2 (\vec{k}\cdot\hat{r}_{12})$$

$$\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)$$

The term with 1 between the second pair of square brackets gives again a_3^s. All remaining integrations are elementary; the final result for a_3^s and a_3 is:

$$a_3^s = \frac{4}{9}\pi^{1/2} n(\beta m)^{-3/2}(k\sigma)^2 g(\sigma)$$

$$a_3 = \frac{2}{3}\pi^{1/2} n(\beta m)^{-3/2}(k\sigma)^2[-4g'(\sigma)j_1(k\sigma)/k+g(\sigma)\{\frac{2}{3} - 2(k\sigma)^{-1}$$

$$\sin k\sigma-4(k\sigma)^{-2}\cos k\sigma+4(k\sigma)^{-3}\sin k\sigma\}] \qquad \text{(F.10)}$$

The moments $M_n^u(k)$ and $M_n^{s,u}(k)$ $(n=0,1,2,3)$ of the hard spheres Ursell expansion can be calculated from (1.32), (1.37), (F.2), (F.4), (F.5), (F.7), (F.8) and (F.10). The moments of $F_k(t)$ are given in (3.10) while the moments of $F_k^s(t)$ agree completely with the exact moments (1.46).

As far as the velocity autocorrelation function is concerned we shall write the two particle term of the hard spheres Ursell expansion as:

$$C_D^{(2)}(t) = \sum_{n=0}^{\infty} a_n^D t^n \qquad \text{(F.11)}$$

From (2.11), (2.33) and (2.35) the following expression for a_1^D follows:

$$a_1^D = \frac{1}{3}\,\beta n^2 (Nm1!)^{-1} \int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \tag{F.12}$$

$$\vec{p}_1 \cdot [L^1(12) - L_o^1(12)] \vec{p}_1$$

Because $L^o(12)-L_o^o(12) = 0$ one sees immediately that

$$a_o^D = 0 \tag{F.13}$$

The coefficient a_1^D is derived from (F.12) as:

$$a_1^D = \frac{1}{3}\,\beta n^2 (Nm)^{-1} \int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \vec{p}_1 \cdot T_+(12) \vec{p}_1$$

$$= \frac{1}{3}\,\beta n^2 (Nm^2)^{-1} \int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) (\vec{p}_{12}\cdot\hat{r}_{12})^2$$

$$(\vec{p}_1 \cdot \hat{r}_{12})\,\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\,\delta(r_{12}-\sigma)$$

All integrations are easy and yield finally for a_1^D:

$$a_1^D = -\frac{8}{3}\pi^{1/2}(\beta m)^{-1/2} n\sigma^2 g(\sigma) \tag{F.14}$$

From (1.38), (2.22), (F.11), (F.13) and (F.14) one derives easily the Ursell moments of $C_D(t)$; it appears that they agree with the exact hard spheres moments (1.47).

APPENDIX G

THE TWO PARTICLE TERMS OF THE URSELL-2 EXPANSION FOR HARD SPHERES

In this appendix a detailed calculation will be given of the two particle terms of the hard spheres Ursell-2 expansion.

a) incoherent intermediate scattering function.

The two particle term $F_k^{s(2)}(t)$ of $F_k^s(t)$ was derived in (3.22) as:

$$F_k^{s(2)}(t) = N^{-1}\sum_\alpha \int_o^t dt_1 \sum_{i=1}^N <\{\exp(-(t-t_1)L_o)\exp(-i\vec{k}\cdot\vec{r}_i)\} \qquad (3.22)$$

$$T_+(\alpha)\exp(t_1L_o)\exp(i\vec{k}\cdot\vec{r}_i)>$$

Taking particle i as particle 1 the summation over i may be replaced by a factor N:

$$F_k^{s(2)}(t) = \sum_\alpha \int_o^t dt_1<\{\exp(-(t-t_1)L_o)\exp(-i\vec{k}\cdot\vec{r}_1)\}$$

$$T_+(\alpha)\exp(t_1L_o)\exp(i\vec{k}\cdot\vec{r}_1)>$$

Because $L_o\vec{r}_1 = \vec{r}_1+\vec{p}_1t/m$ the effect of the free streaming operators leads to:

$$F_k^{s(2)}(t) = \sum_\alpha \int_o^t dt_1<\exp(-i\vec{k}\cdot(\vec{r}_1-\vec{p}_1(t-t_1)/m))T_+(\alpha)$$

$$\exp(i\vec{k}\cdot(\vec{r}_1+\vec{p}_1t_1/m))>$$

The pair of particles α must contain particle 1 to give a non zero contribution; taking for the other particle particle 2 the summation over all pairs α produces only a factor (N-1):

$$F_k^{s(2)}(t) = (N-1)\int_o^t dt_1<\exp(-i\vec{k}\cdot(\vec{r}_1-\vec{p}_1(t-t_1)/m)) \qquad (G.1)$$

$$T_+(12)\exp(i\vec{k}\cdot(\vec{r}_1+\vec{p}_1t_1/m))>$$

Writing the collisional part $T_+(12)$ (1.22) of the hard spheres Liouville operator as:

$$T_+(12) = m^{-1}\sigma^2 \int_{\vec{p}_{12}\cdot\hat{\sigma}<0} d\hat{\sigma}|\vec{p}_{12}\cdot\hat{\sigma}|\delta(\vec{r}_{12}-\vec{\sigma})(b_{12}-1) \qquad (G.2)$$

and using (1.24) and (1.25), the two particle term takes the form:

$$F_k^{s(2)}(t) = (N-1)\int_0^t dt_1 \langle \exp(i\vec{k}\cdot\vec{p}_1(t-t_1)/m)m^{-1}\sigma^2 \int_{\vec{p}_{12}\cdot\hat{\sigma}<0} d\hat{\sigma}|\vec{p}_{12}\cdot\hat{\sigma}|$$

$$\delta(\vec{r}_{12}-\vec{\sigma})[\exp(i\vec{k}\cdot(\vec{p}_1/m-(\vec{p}_{12}/m\cdot\hat{\sigma})\hat{\sigma})t_1)-\exp(i\vec{k}\cdot\vec{p}_1 t_1/m)]\rangle$$

Writing out the ensemble average and introducing center of mass variables $\vec{P}$, $\vec{R}$ and relative variables $\vec{p}$, $\vec{r}$ (2.25) this expression takes the following form:

$$F_k^{s(2)}(t) = n^2(Nm)^{-1}\int_0^t dt_1 \int d\vec{r}d\vec{R}d\vec{p}d\vec{P}\,\Phi(P)\varphi(p)g(r)\exp(i\vec{k}\cdot\vec{P}t/2m)$$

$$\exp(i\vec{k}\cdot\vec{p}(t-t_1)/m)\sigma^2 \int_{\vec{p}\cdot\hat{\sigma}<0} d\hat{\sigma}|2\vec{p}\cdot\hat{\sigma}|\delta(\vec{r}-\vec{\sigma})$$

$$[\exp(i\vec{k}\cdot(\vec{p}-(2\vec{p}\cdot\hat{\sigma})\hat{\sigma})t_1/m)-\exp(i\vec{k}\cdot\vec{p}t_1/m)]$$

The integrations over $\vec{P}$ and $\vec{R}$ are easy and yield:

$$F_k^{s(2)}(t) = m^{-1}n\exp(-k^2t^2/4\beta m)\int_0^t dt_1 \int d\vec{p}d\vec{r}\varphi(p)g(r)$$

$$\exp(i\vec{k}\cdot\vec{p}(t-t_1)/m)\sigma^2 \int_{\vec{p}\cdot\hat{\sigma}<0} d\hat{\sigma}|2\vec{p}\cdot\hat{\sigma}|\delta(\vec{r}-\vec{\sigma})[\exp(i\vec{k}\cdot(\vec{p}-$$

$$(2\vec{p}\cdot\hat{\sigma})\hat{\sigma})t_1/m)-\exp(i\vec{k}\cdot\vec{p}t_1/m)]$$

For simplicity we shall substitute for $\vec{p}$ the relative velocity $\vec{v} = 2\vec{p}/m$:

$$F_k^{s(2)}(t) = n\exp(-k^2t^2/4\beta m)\int_0^t dt_1\int d\vec{v}d\vec{r}\varphi(v)g(r)$$

$$\exp(i\vec{k}\cdot\vec{v}(t-t_1)/2)\sigma^2\int_{\vec{v}\cdot\hat{\sigma}<0} d\hat{\sigma}|\vec{v}\cdot\hat{\sigma}|\delta(\vec{r}-\vec{\sigma})[\exp(i\vec{k}\cdot(\vec{v}/2-$$

$$(\vec{v}\cdot\hat{\sigma})\hat{\sigma})t_1)-\exp(i\vec{k}\cdot\vec{v}t_1/2)]$$

with (G.3)

$$\varphi(v) = (\beta m/4\pi)^{3/2}\exp(-\beta mv^2/4)$$

The integration over $\vec{r}$ can immediately be carried out, yielding:

$$F_k^{s(2)}(t) = n\sigma^2 g(\sigma)\exp(-k^2t^2/4\beta m)\int_0^t dt_1\int d\vec{v}\varphi(v)\exp(i\vec{k}\cdot\vec{v}(t-t_1)/2)$$

$$\int_{\vec{v}\cdot\hat{\sigma}<0} d\hat{\sigma}|\vec{v}\cdot\hat{\sigma}|[\exp(i\vec{k}\cdot\vec{v}'t_1/2)-\exp(i\vec{k}\cdot\vec{v}t_1/2)]$$

where also the post collisional relative velocity $\vec{v}' = \vec{v}-2(\vec{v}\cdot\hat{\sigma})\hat{\sigma}$ has been substituted. Now we replace the integration variable $\hat{\sigma}$ by $\hat{v}'$ ($\vec{v}' = v'\hat{v}'$ with $v' = v$), thus

$$\int_{\vec{v}\cdot\hat{\sigma}<0} d\hat{\sigma}|\vec{v}\cdot\hat{\sigma}| \rightarrow v/4\int d\hat{v}'$$

After the introduction of $\hat{v}'$ the expression for $F_k^{s(2)}(t)$ becomes:

$$F_k^{s(2)}(t) = \frac{1}{4}n\sigma^2 g(\sigma)\exp(-k^2t^2/4\beta m)\int_0^t dt_1\int_0^\infty v^3\varphi(v)dv\int d\hat{v}\int d\hat{v}'$$

$$\exp(i\vec{k}\cdot\vec{v}(t-t_1)/2)\{\exp(i\vec{k}\cdot\vec{v}'t_1/2)-\exp(i\vec{k}\cdot\vec{v}t_1/2)\}$$

The integration over t_1 is easy and yields:

$$F_k^{s(2)}(t) = \frac{1}{4} n\sigma^2 g(\sigma) \exp(-k^2t^2/4\beta m) \int_0^\infty v^3 \varphi(v)\, dv \int d\hat{v} \int d\hat{v}'$$

$$\left[\frac{\exp(i\vec{k}\cdot\vec{v}'t/2) - \exp(i\vec{k}\cdot\vec{v}t/2)}{i\vec{k}\cdot(\vec{v}'-\vec{v})/2} - t \exp(i\vec{k}\cdot\vec{v}t/2) \right]$$

Taking $\vec{k}$ as the polar axis and introducing for $\hat{v}$ and $\hat{v}'$ the polar coordinates (θ,φ) and (θ',φ') we obtain for the two particle term:

$$F_k^{s(2)}(t) = \pi^2 n\sigma^2 g(\sigma) \exp(-k^2t^2/4\beta m) \int_0^\infty v^3 \varphi(v)\, dv \int_0^\pi \sin\theta\, d\theta \int_0^\pi \sin\theta'\, d\theta'$$

$$\left[\frac{\exp(ikv \cos\theta' t/2) - \exp(ikv \cos\theta t/2)}{ikv(\cos\theta' - \cos\theta)/2} - t \exp(ikv \cos\theta t/2) \right]$$

This expression becomes simpler by substituting for θ and θ' the new variables u and w defined by:

$$u - w = \cos\theta$$

$$u + w = \cos\theta'$$

The integration over u can be carried out and the result for the two particle term is:

$$F_k^{s(2)}(t) = 8\pi^2 n\sigma^3 g(\sigma)/(k\sigma) \exp(-k^2t^2/4\beta m) \int_0^\infty v^2 \varphi(v)\, dv$$

$$\left[2\int_0^1 dw\, (kvwt/2)^{-1} \sin(kvwt/2) \sin(kv(1-w)t/2) - \sin(kvt/2) \right]$$

The expression between the square brackets can be rewritten in terms of sine and cosine integrals (Abramowitz, Stegun, 1965) and after the introduction of the following dimensionless variables:

$$v = (\beta m)^{-1/2} u$$
$$\lambda = (\beta m)^{-1/2} kt \qquad \text{(G.4)}$$

the final result for $F_k^{s(2)}(t)$ is:

$$F_k^{s(2)}(t) = \pi^{\frac{1}{2}} n\sigma^3 g(\sigma)(k\sigma)^{-1}\exp(-\lambda^2/4)\lambda^{-1}\int_0^\infty u\exp(-u^2/4)du$$

$$[2\sin(\lambda u/2)Si(\lambda u)+2\cos(\lambda u/2)\{Ci(\lambda u)-\ln(\lambda u)-\gamma\} \qquad (G.5)$$

$$-\lambda u\sin(\lambda u/2)]$$

where γ is Euler's constant.

b) <u>coherent intermediate scattering function.</u>

The two particle term $F_k^{(2)}(t)$ of the coherent intermediate scattering function follows from (3.22) and (3.28) as:

$$F_k^{(2)}(t) = F_k^{s(2)}(t)+N^{-1}\sum_\alpha\sum_{i\neq j}\int_0^t dt_1 <[\exp(-(t-t_1)L_o)\exp(i\vec{k}\cdot\vec{r}_i)]$$

$$T_+(\alpha)\exp(t_1L_o)\exp(i\vec{k}\cdot\vec{r}_j)>$$

Taking for particles i and j resp. particles 1 and 2, the summations over i and j produce merely a factor N(N-1), so:

$$F_k^{(2)}(t) = F_k^{s(2)}(t)+(N-1)\sum_\alpha\int_0^t dt_1 <[\exp(-(t-t_1)L_o)\exp(-i\vec{k}\cdot\vec{r}_1)]$$

$$T_+(\alpha)\exp(t_1L_o)\exp(i\vec{k}\cdot\vec{r}_2)>$$

This becomes after working out the effect of the free streaming operators:

$$F_k^{(2)}(t) = F_k^{s(2)}(t)+(N-1)\sum_\alpha\int_0^t dt_1 <\exp(-i\vec{k}\cdot(\vec{r}_1-\vec{p}_1(t-t_1)/m))$$

$$T_+(\alpha)\exp(i\vec{k}\cdot(\vec{r}_2+\vec{p}_2t_1/m))> \qquad (G.6)$$

To give a non zero contribution to the two particle term the pair α of colliding particles must contain particle 2; for the other particle we can take on the one hand particle 1, on the other hand some other particle, say particle 3.

So we can write the two particle term in the following form:

$$F_k^{(2)}(t) = F_k^{s(2)}(t)+F_k^{A}(t)+F_k^{B}(t)$$

with

$$F_k^{A}(t) = (N-1)\int_o^t dt_1 \langle \exp(-i\vec{k}\cdot(\vec{r}_1-\vec{p}_1(t-t_1)/m)T_+(12)$$

$$\exp(i\vec{k}\cdot(\vec{r}_2+\vec{p}_2 t_1/m)\rangle$$

and (G.7)

$$F_k^{B}(t) = (N-1)(N-2)\int_o^t dt_1 \langle \exp(-i\vec{k}\cdot(\vec{r}_1-\vec{p}_1(t-t_1)/m)$$

$$T_+(23)\exp(i\vec{k}\cdot(\vec{r}_2+\vec{p}_2 t_1/m))\rangle$$

We shall start with $\dot{F}_k^{A}(t)$. Just in the same way as was done for $F_k^{s(2)}(t)$ we can write out the ensemble average, introduce center of mass and relative variables and integrate over the center of mass variables; the result is:

$$F_k^{A}(t) = n\exp(-k^2t^2/4\beta m)\int_o^t dt_1\int d\vec{r}d\vec{v}g(r)\varphi(v)\exp(-i\vec{k}\cdot\vec{r})$$

$$\exp(i\vec{k}\cdot\vec{v}(t-t_1)/2)\sigma^2\int_{\hat{v}\cdot\hat{\sigma}<0} d\hat{\sigma}\left|\vec{v}\cdot\hat{\sigma}\right|\delta(\vec{r}-\vec{\sigma}) \quad \text{(G.8)}$$

$$[\exp(-i\vec{k}\cdot(\vec{v}-2(\vec{v}\cdot\hat{\sigma})\hat{\sigma})t_1/2)-\exp(-i\vec{k}\cdot\vec{v}t_1/2)]$$

The integration over $\vec{r}$ is very simple and yields:

$$F_k^{A}(t) = n\sigma^2 g(\sigma)\exp(-k^2t^2/4\beta m)\int_o^t dt_1\int d\hat{\sigma}\ \exp(-i\vec{k}\cdot\vec{\sigma})\int_{\hat{v}\cdot\hat{\sigma}<0} d\vec{w}\varphi(v)$$

$$\exp(i\vec{k}\cdot\vec{v}(t-t_1)/2)\left|\vec{v}\cdot\hat{\sigma}\right|[\exp(-i\vec{k}\cdot(\vec{v}-2(\vec{v}\cdot\hat{\sigma})\hat{\sigma})t_1/2)$$

$$-\exp(-i\vec{k}\cdot\vec{v}t_1/2)]$$

The integrations over $\vec{v}$ can be carried out by taking $\vec{\sigma}$ as the z-axis. The variables v_x and v_y run from $-\infty$ to ∞ while v_z runs from $-\infty$ to 0 because of $\hat{v}\cdot\hat{\sigma}<0$. The integrations lead to:

$$F_k^A(t) = n\sigma^2 g(\sigma)(\beta m/4\pi)^{\frac{1}{2}}\exp(-k^2t^2/4\beta m)\int_0^t dt_1 \exp(-k^2(t-2t_1)^2/4\beta m)$$

$$\int d\hat{\sigma}\, \exp(-i\vec{k}\cdot\vec{\sigma})\exp((t-2t_1)^2(\vec{k}\cdot\hat{\sigma})^2/4\beta m)\int_0^\infty v_z dv_z \exp(-\beta m v_z^2/4)$$

$$\exp(-\frac{1}{2}i(t-t_1)(\vec{k}\cdot\hat{\sigma})v_z)[\exp(-\frac{1}{2}it_1(\vec{k}\cdot\hat{\sigma})v_z)$$

$$-\exp(\frac{1}{2}it_1(\vec{k}\cdot\hat{\sigma})v_z)]$$

The integral over $\hat{\sigma}$ is carried out by introducing polar coordinates θ,φ for $\hat{\sigma}$ while taking $\vec{k}$ as the polar axis; after the transformation from θ to $u = \cos\theta$ the expression becomes:

$$F_k^A(t) = 2\pi n\sigma^2 g(\sigma)(\beta m/4\pi)^{\frac{1}{2}}\exp(-k^2t^2/4\beta m)\int_0^t dt_1 \exp(-k^2$$

$$(t-2t_1)^2/4\beta m)\int_0^\infty v_z dv_z \exp(-\beta m v_z^2/4)\int_{-1}^{1} du\, \exp(-ik\sigma u)$$

$$\exp(k^2(t-2t_1)^2u^2/4\beta m)\exp(-\frac{1}{2}i(t-t_1)kv_z u)$$

$$\cdot -2i\sin(kv_z u t_1/2)$$

Writing out the exponentionals in sines and cosines and introducing a new variable $t' = t-2t_1$ for t_1 the expression for $F_k^A(t)$ becomes:

$$F_k^A(t) = 2\pi n\sigma^2 g(\sigma)(\beta m/4\pi)^{\frac{1}{2}}\exp(-k^2t^2/4\beta m)\int_{-t}^{t} dt'\exp(-k^2t'^2/4\beta m)$$

$$\int_0^\infty v_z dv_z \exp(-\beta m v_z^2/4)\int_0^1 du\, \exp(k^2t'^2u^2/4\beta m)[\cos(ku(\sigma+v_z t/2))$$

$$-\cos(ku(\sigma+v_z t'/2))]$$

Finally we can replace v_z by a dimensionless velocity $w = (\beta m)^{1/2} v_z$ and t' by a dimensionless time $\tau = t'(\beta m)^{-1/2}/\sigma$, resulting in:

$$F_k^A(t) = \pi^{\frac{1}{2}} n\sigma^3 g(\sigma)\exp(-\lambda^2/4)\, t^* \int_{-1}^{1} d\tau \int_{o}^{1} du\ \exp(-\lambda^2\tau^2(1-u^2)/4)$$
$$\int_{o}^{\infty} w\ dw\ \exp(-w^2/4)[\cos(u(k\sigma+\lambda w/2))-\cos(u(k\sigma+\lambda w\tau/2))] \tag{G.9}$$

where $t^* = t(\beta m)^{-1/2}/\sigma$ and $\lambda = k\sigma t^*$.

Although the expression (G.7) for $F_k^B(t)$ appears more difficult because three particles play a role, we shall show that this part of the two particle term has a very simple form. From (G.7) and (G.2), with (1.2) replaced by (2.3), it follows that

$$F_k^B(t) = (N-1)(N-2)\int_o^t dt_1 \langle \exp(-i\vec{k}\cdot\vec{r}_{12})\exp(i\vec{k}\cdot\vec{p}_1(t-t_1)/m)$$
$$m^{-1}\sigma^2 \int_{\vec{p}_{23}\cdot\hat{\sigma}<0} d\hat{\sigma}\,|\vec{p}_{23}\cdot\hat{\sigma}|\,\delta(\vec{r}_{23}-\vec{\sigma})[\exp(i\vec{k}\cdot(\vec{p}_2-(\vec{p}_{23}\cdot\hat{\sigma})\hat{\sigma})t_1/m)$$
$$-\exp(i\vec{k}\cdot\vec{p}_2 t_1/m)]\rangle$$

Writing out the ensemble average, this becomes:

$$F_k^B(t) = n^3N^{-1}\int_o^t dt_1 \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{p}_1 d\vec{p}_2 d\vec{p}_3 \phi(p_1)\phi(p_2)\phi(p_3) g(\vec{r}_1\vec{r}_2\vec{r}_3)$$
$$\exp(-i\vec{k}\cdot\vec{r}_{12})\exp(i\vec{k}\cdot\vec{p}_1(t-t_1)/m)\, m^{-1}\sigma^2 \int_{\vec{p}_{23}\cdot\hat{\sigma}<o} d\hat{\sigma}\,|\vec{p}_{23}\cdot\hat{\sigma}|\,\delta(\vec{r}_{23}-\vec{\sigma})$$
$$[\exp(i\vec{k}\cdot(\vec{p}_2-(\vec{p}_{23}\cdot\hat{\sigma})\hat{\sigma})t_1/m)-\exp(i\vec{k}\cdot\vec{p}_2 t_1/m)]$$

where the triple correlation function $g(\vec{r}_1\vec{r}_2\vec{r}_3)$ can be derived from (1.5). The integration over $\vec{p}_1$ is easy and yields $\exp(-k^2(t-t_1)^2/2\beta m)$. Furthermore we shall introduce instead of the momenta $\vec{p}_2$ and $\vec{p}_3$ the center of mass momentum $\vec{P}$ and the relative momentum $\vec{p}$ of the particles 2 and 3, defined by:

$$\vec{p}_2+\vec{p}_3 = \vec{P}$$

$$\vec{p}_2-\vec{p}_3 = 2\vec{p}$$

It appears that after this substitution the integration over $\vec{P}$ is simple and there results for $F_k^B(t)$:

$$F_k^B(t) = n^3(Nm)^{-1}\int_o^t dt_1 \exp(-k^2(t-t_1)^2/2\beta m)\exp(-k^2t_1^2/4\beta m)$$

$$\int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 g(\vec{r}_1\vec{r}_2\vec{r}_3)\int d\vec{p}\varphi(p)\exp(-i\vec{k}\cdot\vec{r}_{12})\sigma^2 \int_{\hat{p}\cdot\hat{\sigma}<0} d\hat{\sigma}|2\vec{p}\cdot\hat{\sigma}|$$

$$\delta(\vec{r}_{23}-\vec{\sigma})[\exp(i\vec{k}\cdot(\vec{p}-(2\vec{p}\cdot\hat{\sigma})\hat{\sigma})t_1/m)-\exp(i\vec{k}\cdot\vec{p}t_1/m)]$$

with $\varphi(p)$ given in (2.26).

Introducing for the relative momentum $\vec{p}$ the relative velocity $\vec{v} = 2\vec{p}/m$ as a new variable, and instead of the positions $\vec{r}_2$ and $\vec{r}_3$ the relative positions $\vec{r}$ and $\vec{r}\,'$, defined by

$$\vec{r} = \vec{r}_1-\vec{r}_2$$

$$\vec{r}\,' = \vec{r}_2-\vec{r}_3$$

thereby noticing that the triple correlation function $g(\vec{r}_1\vec{r}_2\vec{r}_3)$ only depends on $|\vec{r}_{12}| = r$, $|\vec{r}_{23}| = r'$ and the angle $\hat{r}_{12}\cdot\hat{r}_{23} = \hat{r}\cdot\hat{r}'$, we arrive for $F_k^B(t)$ at:

$$F_k^B(t) = n^2\int_o^t dt_1\exp(-k^2(t-t_1)^2/2\beta m)\exp(-k^2t_1^2/4\beta m)$$

$$\int d\vec{r} \exp(-i\vec{k}\cdot\vec{r})\int d\vec{r}\,'g(r,r',\hat{r}\cdot\hat{r}')\int d\vec{v}\varphi(v)$$

$$\sigma^2 \int_{\hat{v}\cdot\hat{\sigma}<0} d\hat{\sigma}|\vec{v}\cdot\hat{\sigma}|\delta(\vec{r}\,'-\vec{\sigma})[\exp(i\vec{k}\cdot\vec{v}\,'t_1/2)-\exp(i\vec{k}\cdot\vec{v}t_1/2)]$$

where $\varphi(v)$ was given in (G.3) and the post collisional relative velocity $\vec{v}' = \vec{v}-2(\vec{v}\cdot\hat{\sigma})\hat{\sigma}$ has been substituted.

If we write $d\vec{v} = v^2 dv d\hat{v}$ and interchange the integrations over $\hat{v}$ and $\hat{\sigma}$, the expression for $F_k^B(t)$ becomes:

$$F_k^B(t) = n^2 \int_0^t dt_1 \exp(-k^2(t-t_1)^2/2\beta m)\exp(-k^2 t_1^2/4\beta m)$$

$$\int d\vec{r}\,\exp(-i\vec{k}\cdot\vec{r}) \int d\vec{r}'g(r,r',\hat{r}\cdot\hat{r}') \int_0^\infty v^2\varphi(v)dv\ \sigma^2 \int d\hat{\sigma}\delta(\vec{r}'-\vec{\sigma})$$

$$\int_{\hat{v}\cdot\hat{\sigma}<0} d\hat{v}\,|\vec{v}\cdot\hat{\sigma}|[\exp(i\vec{k}\cdot\vec{v}'/t_1/2)-\exp(i\vec{k}\cdot\vec{v}t_1/2)] \qquad (G.10)$$

The $\hat{v}$-integral may be simplified by introducing in the first term of the integrand $\hat{v}' = \vec{v}'/|\vec{v}'|$ as a new variable and in the second term $-\hat{v}$; this results in:

$$F_k^B(t) = n^2 \int_0^t dt_1 \exp(-k^2(t-t_1)^2/2\beta m)\exp(-k^2 t_1^2/4\beta m)$$

$$\int d\vec{r}\,\exp(-i\vec{k}\cdot\vec{r}) \int d\vec{r}'g(r,r',\hat{r}\cdot\hat{r}') \int_0^\infty v^2\varphi(v)dv\sigma^2 \int d\hat{\sigma}\delta(\vec{r}'-\vec{\sigma})$$

$$\int_{\hat{v}\cdot\hat{\sigma}>0} d\hat{v}\,|\vec{v}\cdot\hat{\sigma}|[\exp(i\vec{k}\cdot\vec{v}t_1/2)-\exp(-i\vec{k}\cdot\vec{v}t_1/2)] \qquad (G.11)$$

The integration over $\hat{v}$ can be performed by expanding the exponentials in spherical harmonics (Merzbacher, 1961):

$$\exp(\pm i\vec{k}\cdot\vec{v}t_1/2) = 4\pi \int_{l=0}^{\infty} \int_{m=-l}^{l} i^l j_l(kvt_1/2) Y^*_{lm}(\pm\hat{k}) Y_{lm}(\hat{v}) \qquad (G.12)$$

where j_l is the l'th order spherical Bessel function, the $*$ means the complex conjugate and Y_{lm} is a spherical harmonic. Substitution of (G.12) in (G.11) leads to:

$$F_k^B(t) = n^2 \int_0^t dt_1 \exp(-k^2(t-t_1)^2/2\beta m)\exp(-k^2 t_1^2/4\beta m) \int d\vec{r}\,\exp(-i\vec{k}\cdot\vec{r})$$

$$\int d\vec{r}'g(r,r',\hat{r}\cdot\hat{r}') \int_0^\infty v^2\varphi(v)dv\ \sigma^2 \int d\hat{\sigma}\delta(\vec{r}'-\vec{\sigma}) \qquad (G.13)$$

$$4\pi \sum_{l=0}^{\infty} \sum_{m=l}^{l} i^l j_l(kvt_1/2)[Y^*_{lm}(\hat{k})-Y^*_{lm}(-\hat{k})] \int_{\hat{v}\cdot\hat{\sigma}>0} d\hat{v}\,|\vec{v}\cdot\hat{\sigma}|Y_{lm}(\hat{v})$$

By taking for $\hat{v}$ the spherical coordinates θ,φ with respect to the polar axis $\vec{\sigma}$ the $\hat{v}$-integral may be written as:

$$\int_{\hat{v}\cdot\hat{\sigma}>0} d\hat{v}\,|\vec{v}\cdot\hat{\sigma}|\,Y_{lm}(\hat{v}) = \int_0^{\pi/2} \sin\theta\, d\theta \int_0^{2\pi} d\varphi\; v\cos\theta\; Y_{lm}(\theta,\varphi)$$

Because Y_{lm} contains a factor $\exp(im\varphi)$ this is zero if $m\neq 0$. After the introduction of a new variable $z = \cos\theta$ and substitution of this expression in (G.13), we obtain for $F_k^B(t)$:

$$F_k^B(t) = n^2\int_0^t dt_1 \exp(-k^2(t-t_1)^2/2\beta m)\exp(-k^2t_1^2/4\beta m)\int d\vec{r}\exp(-i\vec{k}\cdot\vec{r})$$
$$\int d\vec{r}\,'g(r,r',\hat{r}\cdot\hat{r}')\int_0^\infty v^3\varphi(v)dv\;\sigma^2\int d\hat{\sigma}\;\delta(\vec{r}\,'-\vec{\sigma})\cdot 8\pi^2\sum_{l=0}^{\infty} i^l \qquad (G.14)$$
$$\{(2l+1)/4\pi\}^{\frac{1}{2}} j_l(kvt_1/2)[Y^*_{lo}(\hat{k})-Y^*_{lo}(-\hat{k})]\int_0^1 zP_l(z)dz$$

From the properties of Legendre polynomials it follows that $Y_{lm}(-\hat{k}) = (-1)^l Y_{lm}(\hat{k})$, thus

$$\begin{aligned} Y^*_{lo}(\hat{k})-Y^*_{lo}(-\hat{k}) &= 0 \qquad l \text{ even} \\ &= 2Y_{lo}(\hat{k}) \quad l \text{ odd} \end{aligned} \qquad (G.15)$$

Furthermore the integration over z in (G.14) yields a very simple result for l odd:

$$\int_0^1 z\,P_l(z)dz = \frac{1}{2}\int_{-1}^1 z\,P_l(z)dz = \frac{1}{2}\int_{-1}^1 P_1(z)P_l(z)dz = \frac{1}{3}\,\delta_{\ell,1} \qquad (G.16)$$

Inserting (G.15) and (G.16) in (G.14), summing over l and using that

$$Y_{10}(\hat{k}) = \{3/4\pi\}^{\frac{1}{2}}\;\hat{k}\cdot\hat{\sigma}$$

($\vec{\sigma}$ was chosen as the polar axis), we arrive at:

$$F_k^B(t) = 4\pi n^2 i\int_0^t dt_1 \exp(-k^2(t-t_1)^2/2\beta m)\exp(-k^2t_1^2/4\beta m)$$

$$\int d\vec{r}\ \exp(-i\vec{k}\cdot\vec{r})\int d\vec{r}\,'g(r,r',\hat{r}\cdot\hat{r}')\int_0^\infty v^3\varphi(v)j_1(kvt_1/2)dv$$

$$\sigma^2\int d\hat{\sigma}\delta(\vec{r}\,'-\vec{\sigma})(\hat{k}\cdot\hat{\sigma})$$

The integrations over v and t_1 can now be done and result in:

$$F_k^B(t) = \frac{1}{2}\pi^{\frac{1}{2}}n^2 i(\beta m)^{-\frac{1}{2}}t\ \exp(-k^2t^2/4\beta m)\operatorname{erf}(\frac{1}{2}kt(\beta m)^{-\frac{1}{2}})$$

$$\int d\vec{r}\ \exp(-i\vec{k}\cdot\vec{r})\int d\vec{r}\,'g(r,r',\hat{r}\cdot\hat{r}')\sigma^2\int d\hat{\sigma}\delta(\vec{r}\,'-\vec{\sigma})(\hat{k}\cdot\hat{\sigma})$$

where erf is the error function. The integration over $\hat{\sigma}$ is very easy and yields immediately:

$$F_k^B(t) = \frac{1}{2}\pi^{\frac{1}{2}}n^2 i(\beta m)^{-\frac{1}{2}}t\ \exp(-k^2t^2/4\beta m)\operatorname{erf}(\frac{1}{2}kt(\beta m)^{-\frac{1}{2}})$$

$$\int d\vec{r}\ \exp(-i\vec{k}\cdot\vec{r})\int d\vec{r}\,'g(r,r',\hat{r}\cdot\hat{r}')\delta(r'-\sigma)(\hat{k}\cdot\hat{r}') \qquad (G.17)$$

To get rid of the triple correlation function we make use of a relation, derived by Konijnendijk and van Leeuwen (1973, appendix A):

$$n\int d\vec{r}\,'\delta(r'-\sigma)\hat{r}'g(r,r',\hat{r}\cdot\hat{r}') = -g'(r)\hat{r}+g(\sigma)\delta(r-\sigma)\hat{r} \qquad (G.18)$$

Because $g'(r) = 0$ for $r < \sigma$ and $g'(r)$ has a δ-singularity at $r = \sigma$ associated with the jump from zero to $g(\sigma)$ in $g(r)$, one sees immediately that the following relation holds for hard spheres:

$$g'(r) - g(\sigma)\delta(r-\sigma) = g'(r)\theta(r-\sigma) \qquad (G.19)$$

After the substitution of (G.18) and (G.19) in (G.17) the expression for $F_k^B(t)$ becomes:

$$F_k^B(t) = -\frac{1}{2}\pi^{\frac{1}{2}} n i(\beta m)^{-\frac{1}{2}} t \exp(-k^2 t^2/4\beta m)\,\mathrm{erf}(\frac{1}{2} kt(\beta m)^{-\frac{1}{2}})$$

$$\int d\vec{r} \exp(-i\vec{k}\cdot\vec{r}) g'(r)\theta(r-\sigma)\hat{k}\cdot\hat{r}$$

Integrating this partially and making use of (1.8) and (1.9) one gets as the final result of the calculation:

$$F_k^B(t) = \frac{1}{2}\pi^{\frac{1}{2}} kt(\beta m)^{-\frac{1}{2}} \exp(-k^2 t^2/4\beta m)\,\mathrm{erf}(\frac{1}{2} kt(\beta m)^{-\frac{1}{2}})$$

$$[4\pi n\sigma^3 (k\sigma)^{-1} j_1(k\sigma) g(\sigma) + S(k) - 1] \tag{G.20}$$

APPENDIX H

THE MOMENTS OF THE HARD SPHERES URSELL-2 EXPANSION

The coherent and incoherent intermediate scattering functions in the Ursell-2 expansion were in chapter 3.4 ((3.20) and (3.27)) derived as:

$$F_k^s(t) = F_k^{s(1)}(t) + F_k^{s(2)}(t)$$

and (H.1)

$$F_k(t) = F_k^{(1)}(t) + F_k^{(2)}(t)$$

with the free streaming parts $F_k^{s(1)}(t)$ and $F_k^{(1)}(t)$ given by (3.23) and (3.29):

$$F_k^{s(1)}(t) = \exp(-k^2t^2/2\beta m) = 1-k^2t^2/2\beta m+...$$

and (H.2)

$$F_k^{(1)}(t) = S(k)\exp(-k^2t^2/2\beta m) = S(k)-S(k)k^2t^2/2\beta m+...$$

To obtain the moments of the Ursell-2 expansion we expand the two particle terms $F_k^{s(2)}(t)$ and $F_k^{(2)}(t)$ in a power series in t:

$$F_k^{s(2)}(t) = \sum_{n=0}^{\infty} a_n^s t^n/n!$$

and (H.3)

$$F_k^{(2)}(t) = \sum_{n=0}^{\infty} a_n t^n/n!$$

where the expansion coefficients a_n^s and a_n may be written as:

$$a_n^s = \left(\frac{\partial^n}{\partial t^n} F_k^{s(2)}(t)\right)_{t=0}$$

and (H.4)

$$a_n = \left(\frac{\partial^n}{\partial t^n} F_k^{(2)}(t)\right)_{t=0}$$

For the two particle terms in appendix G ((G.1) and (G.6)) the following expressions were derived:

$$F_k^{s(2)}(t) = (N-1)\int_o^t dt_1 \langle \exp(-i\vec{k}\cdot(\vec{r}_1-\vec{p}_1(t-t_1)/m))T_+(12)$$

$$\exp(i\vec{k}\cdot(\vec{r}_1+\vec{p}_1 t_1/m))\rangle$$

and (H.5)

$$F_k^{(2)}(t) = F_k^{s(2)}(t)+(N-1)\sum_\alpha \int_o^t dt_1 \langle \exp(-i\vec{k}\cdot(\vec{r}_1-\vec{p}_1(t-t_1)/m))$$

$$T_+(\alpha)\exp(i\vec{k}\cdot(\vec{r}_2+\vec{p}_2 t_1/m))\rangle$$

In the last expression the pair α must contain particle 2 to give a non zero contribution to $F_k^{(2)}(t)$. We shall now give a detailed calculation of the first moments.

a) <u>zeroth moment</u>

It is clear that

$$F_k^{s(2)}(0) = F_k^{(2)}(0) = 0$$

thus the zeroth moments follow immediately from (H.1)-(H.4) as:

$$M_o^s(k) = 1$$

and (H.6)

$$M_o(k) = 1$$

b) <u>first moment</u>

Taking the first derivative of $F_k^{s(2)}(t)$ at t = 0 yields immediately for the coefficient a_1^s:

$$a_1^s = (N-1)\langle \exp(-i\vec{k}\cdot\vec{r}_1)T_+(12)\exp(i\vec{k}\cdot\vec{r}_1)\rangle$$

From (1.22) and (1.24) one sees that $T_+(12)$ gives a vanishing result if this operator works on a function of the position variables only, so that

$$a_1^s = 0$$

In the same way one sees that

$$a_1 = 0$$

Because the free streaming parts (H.2) are even in t it is clear that the first moments vanish:

$$M_1^s(k) = 0$$

and (H.7)

$$M_1(k) = 0$$

c) <u>second moment</u>

Taking the second derivative of (H.5) at t = 0 one sees that the only nonvanishing part of a_2^s is given by:

$$a_2^s = (N-1)\langle T_+(12)i\vec{k}\cdot\vec{p}_1/m\rangle$$

which can, with the aid of (1.22), (1.24) and (1.25), also be written as:

$$a_2^s = (N-1)im^{-2}\langle(\vec{p}_{12}\cdot\hat{r}_{12})^2(\vec{k}\cdot\hat{r}_{12})\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)\rangle$$

This yields zero because of the isotropy of the system, so:

$$a_2^s = 0 \tag{H.8}$$

and (H.1)-(H.3) yield for the second moment of $F_k^s(t)$:

$$M_2^s(k) = -k^2/\beta m \tag{H.9}$$

The coefficient a_2 follows from (H.4), (H.5) and (H.8) as:

$$a_2 = (N-1)\sum_{i\neq 2}\langle\exp(-i\vec{k}\cdot\vec{r}_{12})T_+(2i)i\vec{k}\cdot\vec{p}_2/m\rangle$$

For particle i we can take particle 1 or some other particle, say particle 3, so that the expression for a_2 becomes:

$$\begin{aligned} a_2 &= (N-1)\langle\exp(-i\vec{k}\cdot\vec{r}_{12})T_+(12)i\vec{k}\cdot\vec{p}_2/m\rangle \\ &\quad +(N-1)(N-2)\langle\exp(i\vec{k}\cdot\vec{r}_{12})T_+(23)i\vec{k}\cdot\vec{p}_2/m\rangle \\ &= A+B \end{aligned} \tag{H.10}$$

where A represents the contribution of the pair (12) and B the contribution of (23).

Writing out the ensemble average and working out the effect of $T_+(12)$ one sees that A can be written as:

$$A = -n^2 i(Nm^2)^{-1}\int d\vec{p}_1 d\vec{p}_2 d\vec{r}_1 d\vec{r}_2 \phi(p_1)\phi(p_2)g(r_{12})\exp(-i\vec{k}\cdot\vec{r}_{12})$$
$$(\vec{p}_{12}\cdot\hat{r}_{12})^2(\vec{k}\cdot\hat{r}_{12})\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)$$

All integrations are easy and yield:

$$A = -4\pi n g(\sigma)(\beta m k)^{-1}(k\sigma)^2 j_1(k\sigma) \qquad \text{(H.11)}$$

with $j_1(k\sigma)$ the first order spherical Bessel function.

The second term B of (H.10) is more complicated; writing out the ensemble average and taking into account the effect of $T_+(23)$ we obtain for B:

$$B = in^3(Nm^2)^{-1}\int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{p}_1 d\vec{p}_2 d\vec{p}_3 \phi(p_1)\phi(p_2)\phi(p_3) g(\vec{r}_1\vec{r}_2\vec{r}_3)$$

$$\exp(-i\vec{k}\cdot\vec{r}_{12})(\vec{p}_{23}\cdot\hat{r}_{23})^2(\vec{k}\cdot\hat{r}_{23})\theta(-\vec{p}_{23}\cdot\vec{r}_{23})\delta(r_{23}-\sigma)$$

The integration over $\vec{p}_1$ yields unity; the integrations over $\vec{p}_2$ and $\vec{p}_3$ may be performed by introducing new variables $\vec{p}$ and $\vec{P}$, defined by:

$$\vec{P} = \vec{p}_2+\vec{p}_3$$

$$\vec{p} = \frac{1}{2}(\vec{p}_2-\vec{p}_3)$$

After the momentum integrations the expression for B becomes:

$$B=in^3(N\beta m)^{-1}\int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 g(\vec{r}_1\vec{r}_2\vec{r}_3)\exp(-i\vec{k}\cdot\vec{r}_{12})(\vec{k}\cdot\hat{r}_{23})\delta(r_{23}-\sigma)$$

The integration over $\vec{r}_3$ can be done by making use of the following integral relation for the triple distribution function (only valid for hard spheres) (Konijnendijk, van Leeuwen, 1973):

$$n\int dr_3\delta(r_{23}-\sigma)\vec{k}\cdot\hat{r}_{23}g(\vec{r}_1\vec{r}_2\vec{r}_3) = \vec{k}\cdot\hat{r}_{12}[-g'(r_{12})+g(\sigma)\delta(r_{12}-\sigma)] \qquad \text{(H.12)}$$

resulting in the following expression for B:

$$B = -in(\beta m)^{-1}\int d\vec{r}\ \exp(-i\vec{k}\cdot\vec{r})(\vec{k}\cdot\hat{r})[g'(r)-g(\sigma)\delta(r-\sigma)]$$

The term with $g(\sigma)\delta(r-\sigma)$ yields $-A$, with A given in (H.11). Remembering that

$$\vec{k}\cdot\hat{r}g'(r) = \vec{k}\cdot\frac{\partial}{\partial\vec{r}}(g(r)-1)$$

it is clear that, after one partial integration, B can be written as:

$$B = -A+nk^2(\beta m)^{-1}\int d\vec{r}\ \exp(-i\vec{k}\cdot\vec{r})(g(r)-1)$$

Adding A and B together and using (1.9) one sees that the final result for a_2 is:

$$a_2 = k^2(S(k)-1)/\beta m$$

and that (H.1)-(H.3) yield for the second moment $M_2(k)$:

$$M_2(k) = -k^2/\beta m \qquad \text{(H.13)}$$

which is in agreement with the exact second moment.

d) <u>third moment</u>

The third derivative of $F_k^{s(2)}(t)$ (H.5) at $t = 0$ yields for the coefficient a_3^s:

$$a_3^s = -(N-1)\langle T_+(12)(\vec{k}\cdot\vec{p}_1/m)^2\rangle$$

$$-(N-1)\langle(\vec{k}\cdot\vec{p}_1/m)T_+(12)(\vec{k}\cdot\vec{p}_1/m)\rangle$$

The first term of this expression was already discussed in appendix F (the term in (F.9) with $T_+(12)L_o(12)$ and $j = 1$). It was seen there that this term gives a vanishing contribution.

Writing out the ensemble average in the second term and working out the effect of the collisional part $T_+(12)$ of the Liouville operator, a_3^s becomes:

$$a_3^s = -n^2(Nm^3)^{-1}\int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12})(\vec{k}\cdot\vec{p}_1)(\vec{p}_{12}\cdot\hat{r}_{12})^2$$

$$(\vec{k}\cdot\hat{r}_{12})\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)$$

After doing the integrations and using (H.1)-(H.3) one gets the following expression for the hard spheres third moment:

$$M_3^s(k) = a_3^s = \frac{8}{3}\pi^{1/2} n(\beta m)^{-3/2}(k\sigma)^2 g(\sigma) \qquad \text{(H.14)}$$

The coefficient a_3 follows from the third derivative of $F_k^{(2)}(t)$ (H.5) at t = 0 as:

$$a_3 = a_3^s + (N-1)\sum_{i\neq 2} \langle \exp(-i\vec{k}\cdot\vec{r}_{12}) T_+(2i)(i\vec{k}\cdot\vec{p}_2/m)^2\rangle + (N-1)\sum_{i\neq 2}$$

$$\langle \exp(-i\vec{k}\cdot\vec{r}_{12})(i\vec{k}\cdot\vec{p}_1/m) T_+(2i)(i\vec{k}\cdot\vec{p}_2/m)\rangle$$

The second term in this expression disappears for the same reason as in appendix F (F.9) the term with $T_+(12)L_o(12)$. In the third term only the pair (12) gives a nonvanishing contribution because of the presence of the factor $(i\vec{k}\cdot\vec{p}_1/m)$. Writing out the ensemble average and taking into account the effect of $T_+(12)$, a_3 becomes:

$$a_3 = a_3^s + n^2(Nm^3)^{-1}\int d\vec{r}_1 d\vec{r}_2 d\vec{p}_1 d\vec{p}_2 \phi(p_1)\phi(p_2) g(r_{12}) \exp(-i\vec{k}\cdot\vec{r}_{12})$$

$$(\vec{k}\cdot\vec{p}_1)(\vec{p}_{12}\cdot\hat{r}_{12})^2\theta(-\vec{p}_{12}\cdot\vec{r}_{12})\delta(r_{12}-\sigma)(\vec{k}\cdot\hat{r}_{12})$$

All integrations can be done and yield with (H.1)-(H.3) finally for the third moment:

$$M_3(k) = a_3 = \frac{8}{3}\pi^{1/2} n(\beta m)^{-3/2} g(\sigma)[(k\sigma)^2 - 3k\sigma \sin k\sigma$$

$$-6\cos k\sigma + 6(k\sigma)^{-1} \sin k\sigma] \qquad (H.15)$$

Comparing the in this appendix derived moments of the hard spheres Ursell-2 expansion ((H.6), (H.7), (H.9), (H.13)-(H.15)) with the exact hard spheres moments (1.45) and (1.46), one sees that the corresponding moments all agree with each other.

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SUMMARY

In this thesis the dynamical behaviour of the atoms in a fluid or gas is studied with time dependent correlation functions as the density-density correlation function and the velocity autocorrelation function. Theoretically it is not possible to calculate these correlation functions exactly for the whole time domain. An exact calculation is only possible for times small with respect to the duration of the collision (see Ch. 1), by using the moments expansion, and for times large with respect to the mean free time by solving the hydrodynamical equations.

In chapter 2 a method is described, the Ursell expansion, which makes it possible to calculate the correlation functions for times up to the mean free time. Experimentally the density-density correlation function is known on this time scale from neutron scattering on noble gases with a low density.

In the Ursell expansion the successive terms describe the effect of an increasing number of colliding particles. For times smaller than the mean free time the most dominant contribution to the correlation functions comes from those collisions in which not more as two particles are involved. In chapter 2 a detailed expression for the two particle term is derived. It is shown, that due to an approximation for the static three particle correlation function, the moments of the two particle term do not agree completely with the exact moments. Therefore for continuous potentials another expansion, the second derivative expansion, is derived; in this new expansion the two particle term has the exact moments.

Chapter 3 gives the Ursell expansion for the case of a hard spheres interaction; the advantage of this interaction is that the mathematical expressions, that describes the collision, are very easy. Because the moments of the two particle term do not agree with the exact moments, another expansion, the Ursell-2 expansion, will be derived. This expansion is only valid for hard spheres and reproduces the exact moments. At the end of chapter 3 the results of calculations on the hard spheres system are presented. It is

shown that both expansions agree very well with molecular dynamics calculations.

Chapter 4 contains the results of calculations on a system with a Lennard-Jones interaction. It appears that both the Ursell expansion and the second derivative expansion agree very well with molecular dynamics calculations of the incoherent intermediate scattering function. The discrepancy between the theoretically calculated coherent intermediate scattering function and the experimental scattering function is substantial. This may be due to the large experimental error, which is of the same order of magnitude as the deviation of the correlation function from its ideal gas value.

SAMENVATTING

In dit proefschrift wordt het dynamisch gedrag van de atomen in een vloeistof of gas onderzocht met behulp van tijdsafhankelijke correlatiefuncties zoals de dichtheids-dichtheidscorrelatiefuncties en de snelheidsautocorrelatiefunctie. Theoretisch is het niet mogelijk deze correlatiefuncties exact te berekenen in het hele tijdsdomein. Een exacte berekening is wel mogelijk voor tijden, die klein zijn ten opzichte van de duur van een botsing (zie hoofdstuk 1), met behulp van de momentenontwikkeling en voor tijden, die groot zijn ten opzichte van de gemiddelde vrije tijd (tussen botsingen), door de hydrodynamische vergelijkingen op te lossen.

In hoofdstuk 2 wordt een methode beschreven, de Ursellontwikkeling, waarmee het mogelijk is de correlatiefuncties te berekenen tot tijden van de orde van grootte van de gemiddelde vrije tijd. Experimenteel is de dichtheids-dichtheidscorrelatiefunctie op deze tijdsschaal bekend uit de neutronenverstrooiing aan edelgassen met een lage dichtheid.

In de Ursellontwikkeling beschrijven de opeenvolgende termen het effect van een toenemend aantal botsende deeltjes. Aangezien voor tijden kleiner dan de gemiddelde vrije tijd de meest dominante bijdrage tot de correlatiefuncties wordt geleverd door die botsingen, waarbij hoogstens twee deeltjes betrokken zijn, wordt in hoofdstuk 2 een expliciete uitdrukking voor de twee-deeltjesterm afgeleid. Aangetoond wordt dat, tengevolge van een benadering voor de statische drie-deeltjescorrelatiefunctie, de momenten van de twee-deeltjesterm niet geheel in overeenstemming zijn met de exacte momenten. Daarom wordt voor continue potentialen ook een andere ontwikkeling, de tweede-afgeleide ontwikkeling, afgeleid, waarvan de twee-deeltjesterm wel de exacte momenten heeft.

Hoofdstuk 3 geeft de Ursellontwikkeling voor het geval van de harde bollen interactie; het voordeel van deze wisselwerking is dat de mathematische uitdrukkingen, die de botsing beschrijven, erg eenvoudig zijn. Omdat de momenten van de twee-deeltjesterm niet overeenstemmen met de exacte momenten, wordt, speciaal voor harde bollen, een andere ontwikkeling, de Ursell-2 ontwikkeling, gegeven, die wel de exacte momenten reproduceert. Aan het eind van hoofdstuk 3 worden de resultaten van berekeningen aan een harde bollen systeem gepresenteerd, waarbij wordt aangetoond dat beide ontwikkelingen goed overeenkomen met de resultaten van moleculaire dynamica berekeningen.

Hoofdstuk 4 bevat de resultaten van berekeningen voor het geval van een Lennard-Jones interactie. Het blijkt dat zowel de Ursell-ontwikkeling als de tweede-afgeleide ontwikkeling zeer goed overeenkomen met moleculaire dynamica berekeningen van de incoherente intermediaire verstrooiingsfunctie. De theoretisch berekende coherente intermediaire verstrooiingsfunctie komt daarentegen slecht overeen met de experimentele verstrooiingsfunctie, wat waarschijnlijk te wijten is aan de grote meetfout, die van dezelfde orde van grootte is als de deviatie van de correlatiefunctie ten opzichte van de ideale gas waarde.

STELLINGEN

I

Een theorie, die het korte tijdsgedrag van correlatiefuncties beschrijft, kan, ondanks het feit dat de tweede en hogere orde momenten niet overeenstemmen met de exakte momenten, toch bevredigende resultaten opleveren.

Dit proefschrift Ch. 3.5 en 4.

II

Bij neutronenverstrooiingsexperimenten dient ervoor gewaakt te worden dat het te meten effect, zoals de deviatie van een correlatiefunctie ten opzichte van de ideale gaswaarde, groter is dan de meetfouten.

Dit proefschrift Ch. 4.

III

Het gebruik van het woord scattering law of verstrooiingswet is misplaatst.

W. Marshall, S.W. Lovesey, Theory of thermal neutron scattering.

IV

Voor het bepalen van de trajectorie van een deeltje in een centraal krachtveld is de Hamilton-Jacobi theorie weinig zinvol.

H. Goldstein, Classical mechanics.

V

De resultaten van de berekeningen van de snelheidsautocorrelatiefunctie met behulp van moleculaire dynamica zijn voor lange tijden discutabel.

W.W. Wood, Fundamental problems in statistical mechanics III,
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VI

Het gebruiken van programma's en subroutines uit de numerieke bibliotheken, die in de meeste rekencentra aanwezig zijn, dient met de uiterste voorzichtigheid te geschieden.

VII

Het effect van moderne audio-visuele hulpmiddelen op het leerproces is nihil wanneer de temperatuur in colloquium- en collegezalen niet bevredigend geregeld kan worden.

VIII

De veiligheid van het spoorwegverkeer zou nog toenemen als er na het koppelen en loskoppelen van wagens of treinstellen altijd een remproef werd gedaan.

IX

De kwaliteit van het openbaar vervoer neemt belangrijk toe als de aankomst- en vertrektijden van streekbussen beter afgestemd worden op resp. de vertrek- en aankomsttijden van treinen.

X

De gemeente dient de betalers van hondenbelasting te specificeren waarvoor de opbrengsten van deze belasting gebruikt worden.

XI

De werkzaamheden van de Organisatie ter Verbetering van de Binnenvisserij dienen erop gericht te zijn de inheemse visstand zo goed mogelijk in stand te houden; dit wordt niet bevorderd door het kweken en uitzetten van uitheemse vissoorten, zoals de graskarper.