

1989

Fast Sound Propagation in Binary Fluid Mixtures

Alessandro Campa

Follow this and additional works at: http://digitalcommons.rockefeller.edu/student_theses_and_dissertations



Part of the [Life Sciences Commons](#)

Recommended Citation

Campa, Alessandro, "Fast Sound Propagation in Binary Fluid Mixtures" (1989). *Student Theses and Dissertations*. 364.
http://digitalcommons.rockefeller.edu/student_theses_and_dissertations/364

This Thesis is brought to you for free and open access by Digital Commons @ RU. It has been accepted for inclusion in Student Theses and Dissertations by an authorized administrator of Digital Commons @ RU. For more information, please contact mcsweej@mail.rockefeller.edu.



FAST SOUND PROPAGATION

IN BINARY FLUID MIXTURES

A thesis submitted to the faculty of the Rockefeller University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy.

by

Alessandro Campa

March 31, 1989.

The Rockefeller University.

New York.

Acknowledgments

I am very much indebted to my advisor, Professor E. G. D. Cohen. His experience has been of great help to me during the development of the work that has resulted in this thesis. I am also very grateful to Dr. I. M. de Schepper for his careful reading of this thesis and his kind hospitality in Delft.

I have greatly enjoyed my friendship with Vlado Rahal and Cherif Hamzaoui and my scientific collaboration with them, and I would like to thank Professor N. N. Khuri, Professor A. I. Sanda, and Dr. H. C. Ren for their interest in our results.

I want to thank the following people for what they have done for me, in different ways, during my stay at The Rockefeller University: Martin Burschka, Andrea Giansanti, Mrs. Bozenka Glatt, Behzad Kamgar-Parsi, Michael McGuigan, Petar Simic, and my former advisor Professor Alexander Tenenbaum.

The constant support from my loved ones goes beyond what can be expressed in words.

ABSTRACT

In this thesis I am concerned with the dynamical properties, at the molecular level, of binary fluid mixtures in equilibrium; binary fluid mixtures are fluids consisting of two different components. As for simple (one component) fluids, the main experimental probes for the study of these properties of binary mixtures are light and neutron scattering.

To connect the dynamics with scattering experiments one can use the kinetic theory of fluids. I have applied the kinetic theory to binary mixtures where the atomic masses of the molecules of the two components are very different (disparate-mass binary mixtures). I have studied both dilute (gaseous) mixtures and dense mixtures.

In the description of the dynamics of the fluid through the density-density correlation functions, one can introduce modes, which can be thought of as the different channels by which the correlations decay in time. Some modes are propagating, in the sense that they describe propagating, and damped, processes. Others are not propagating, and describe diffusive, purely damped processes.

The results concern the appearance of a fast propagating mode, in disparate-mass binary mixtures, in a vast range of densities, from dilute gas mixtures to rather high (liquid) densities. This fast mode appears beyond the hydrodynamic regime. One can call this mode fast sound, because, like ordinary sound, it propagates, but it is faster. The most important point is that the fast sound is associated with the dynamics of the light component only. In the thesis I explain how this phenomenon could be observed in light and neutron scattering experiments. If it is detected in actual scattering experiments on disparate-mass binary mixtures it would be the first time that a non hydrodynamic mode in a fluid is clearly "seen".

CONTENTS

Chapter 1	Correlation functions and scattering experiments	1
1.1	Correlation functions, light and neutron scattering	2
1.2	Kinetic theories	17
1.3	Outline of later chapters	24
Chapter 2	Kinetic theory of correlation functions	28
2.1	Kinetic equation	28
2.2	The BGK method	39
2.3	Extension to binary mixtures	42
2.4	Simple fluid limit	51
Chapter 3	The computation	67
3.1	The matrix elements of the mean field operator	68
3.2	The matrix elements of the collision operator	68
3.3	The matrix $A(k, z)$	72
3.4	The static structure factors $S_{ij}(k)$	74
3.5	The velocity of sound and the χ_{ij}	76

Chapter 4	The results	78
4.1	Some previous results on disparate-mass binary mixtures	80
4.2	Neutron scattering and light scattering in disparate-mass mixtures	81
4.3	Fast sound propagation: an introduction	85
4.4	Dilute mixtures: light scattering and polarizabilities	90
4.5	H ₂ -Ar mixtures	92
4.6	Other mixtures	108
4.7	Dense fluids: neutron scattering	109
4.8	He-Xe mixtures	113
4.9	Other mixtures	118
Chapter 5	Conclusions	121
5.1	Discussion	121
5.2	Open questions	123
Appendix I		125
Appendix II		127
References		129

Correlation functions and scattering experiments

Physics of fluids is a challenging subject that has received much interest. With fluids I indicate both gases and liquids. Both equilibrium and non equilibrium properties of fluids are important fields of application of statistical mechanics, which provides a relation between, on the one hand, the interaction laws among the fluid particles, and, on the other hand, the macroscopic properties of the fluid.

In this thesis I am concerned with the dynamical properties, at the molecular level, of binary fluid mixtures in equilibrium; binary fluid mixtures are fluids consisting of two different components. As for simple (one component) fluids, the main experimental probes for the study of these properties of binary mixtures are light and neutron scattering.

In the first section of this chapter I will describe the theoretical treatment of fluids in equilibrium and I will briefly outline how from scattering experiments one can get information on the dynamics on the molecular scale in the fluid. To connect the dynamics with scattering experiments I have used the kinetic theory of fluids: therefore in the second section a short historical summary will be given of the development of kinetic theory in the last several years. In the last section I will give an outline of the contents of later chapters and I will mention the most important part of the results.

1.1 Correlation functions, light and neutron scattering

The fundamental laws that describe atoms and molecules are quantum mechanical, but in the study of the dynamical properties of fluids at not too low temperatures it is sufficient to use classical mechanics. A rule of thumb to estimate the importance of quantum effects is to compare the thermal wavelength $\Lambda = h/\sqrt{2\pi mk_B T}$ (where m is the mass of a particle, k_B the Boltzmann constant, T the absolute temperature and h the Planck constant) with the average interparticle distance: if the former is considerably smaller than the latter, then a classical treatment is sufficient. This holds for atomic or molecular gases and liquids at temperatures not too close to absolute zero. In addition, when we study dynamical properties, quantum effects are negligible, if we consider times considerably larger than $\hbar/k_B T$ ($\hbar = h/2\pi$). In general this condition is more stringent than the first one, and quantum effects manifest themselves in fluids made of light atoms like neon [1]. When comparing experimental results with theoretical predictions based on a classical theory, there are procedures, in the analysis of experimental data, that can be applied to correct for quantum effects. The possibility to estimate the quantum corrections and the fact that these, at the conditions considered here, are not dominant, gives confidence in using classical statistical physics, as I will do in this thesis.

The dynamics of fluids in equilibrium is usually described in the language of time correlation functions. They are defined in this section. But first one has to introduce the canonical average of dynamical variables.

1.1.1.1 Dynamical variables

The dynamical variables considered here depend on the phase space (namely on the coordinates and velocities [2] of some or all the particles of the fluid) and in addition on a coordinate field variable \vec{r} ; they also depend implicitly on time through the phase space variables, which can be collectively indicated with $\Gamma(t)$. So for a generic dynamical variable \hat{A} :

$$\hat{A} = \hat{A}(\vec{r}, \Gamma(t))$$

In systems at equilibrium one can perform the usual canonical average, defined by:

$$A(\vec{r}, t) = \langle \hat{A}(\vec{r}, \Gamma(t)) \rangle_N = \frac{1}{Z(\beta, V, N)} \int d\Gamma \hat{A}(\vec{r}, \Gamma(t)) e^{-\beta H(\Gamma)}$$

where $H(\Gamma)$ is the hamiltonian of the system with N particles in a volume V , $\beta=1/k_B T$, and $Z(\beta, V, N)$ is the partition function:

$$Z(\beta, V, N) = \int d\Gamma e^{-\beta H(\Gamma)}$$

From the properties of the canonical ensemble it follows that $A(\vec{r}, t)$ actually does not depend on t . In fact, we have:

$$\hat{A}(\vec{r}, \Gamma(t)) = e^{tL} \hat{A}(\vec{r}, \Gamma(0))$$

where L is the Liouville operator, which acts on the phase space variables Γ (from now on Γ means $\Gamma(0)$); e^{tL} is the time evolution operator that transforms $\Gamma(0)$ into $\Gamma(t)$: $e^{tL}\Gamma(0) = \Gamma(t)$. L is antihermitian, and we also have the property $Le^{-\beta H(\Gamma)}=0$, so that:

$$\begin{aligned} \int d\Gamma \hat{A}(\vec{r}, \Gamma(t)) e^{-\beta H(\Gamma)} &= \int d\Gamma (e^{tL} \hat{A}(\vec{r}, \Gamma(0))) e^{-\beta H(\Gamma)} = \\ &= \int d\Gamma \hat{A}(\vec{r}, \Gamma(0)) e^{-tL} e^{-\beta H(\Gamma)} = \int d\Gamma \hat{A}(\vec{r}, \Gamma(0)) e^{-\beta H(\Gamma)}; \end{aligned}$$

therefore:

$$A(\vec{r}, t) = A(\vec{r}, 0) = A(\vec{r}).$$

As an example we can take the variable:

$$\hat{n}(\vec{r}, \Gamma) = \sum_{p=1}^N \delta(\vec{r} - \vec{r}_p) \quad (1.1)$$

(where $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N$ are the coordinates of the N particles in the fluid) whose canonical average gives the local density:

$$n(\vec{r}) = \langle \hat{n}(\vec{r}, \Gamma) \rangle_N.$$

The fluid will be considered homogeneous and isotropic. The reason for this is the following. Strictly speaking, only a fluid in absence of an external field is homogeneous and isotropic; the presence of the walls of the container that encloses the fluid causes a departure from this situation only in a very narrow layer near the walls, which can be neglected under most practical conditions. Also in spite of the laboratory gravitational field, the fluid can be considered practically homogeneous and isotropic; in fact we can take $k_B T$ as a typical average value of the kinetic energy of a particle, while as a typical value for the variation of its gravitational potential energy we can take mgd , where g is the acceleration of gravity and d is the linear dimension of the container. Their ratio, $mgd/k_B T$, even for a heavy particle like a Xenon atom, and for a low temperature of about 50 °K, is around 3×10^{-3} , if we assume $d \approx 100$ cm. Mathematically the walls, are represented by a very sharply peaked external potential. One could get rid of this surface effect only in the thermodynamic limit, $N \rightarrow \infty$, $V \rightarrow \infty$ with N/V constant. The alternative approach which is most often used is one in which one does not take the true thermodynamic limit, i. e. N and V are not sent to infinity, but the wall potential is neglected. There are some practical consequences of this approach. For example, due to the very large value of the linear dimension of V with respect to the interparticle distance, each time that in an integral of the type $\int d\vec{r} f(\vec{r})$ a function $f(\vec{r})$ appears that decays to zero within a typical range of the order of the interparticle

distance [3], then the limits of integration can be sent to infinity; but we keep $\int d\vec{r} = V$. This is used, for example, in the next subsection in the expression of the space Fourier transform of $C_{AB}(\vec{r}, t)$ defined by (1.2).

From now on, the fluid will be considered homogeneous and isotropic. In a homogeneous system $A(\vec{r})$ does not depend on \vec{r} ; in particular:

$$n(\vec{r}) = n = \frac{N}{V}$$

where n is the uniform density of the fluid.

1.1.2 Space time correlation functions

A space time correlation function between two dynamical variables \hat{A} and \hat{B} is defined by:

$$C_{AB}(\vec{r}, t) = V \langle \hat{A}(\vec{r}', \Gamma(0)) \hat{B}(\vec{r} + \vec{r}', \Gamma(t)) \rangle_N \quad (1.2)$$

The factor of proportionality V is convenient for the specific functions that will be considered later. C_{AB} , for fixed \vec{r} , does not depend on \vec{r}' , because of the homogeneity of the fluid. From the isotropy we have that it actually depends only on $r = |\vec{r}|$. We have the following asymptotic properties, for short range interparticle potentials:

$$\lim_{|\vec{r}| \rightarrow \infty} C_{AB}(\vec{r}, t) = \lim_{t \rightarrow \infty} C_{AB}(\vec{r}, t) = V \langle \hat{A} \rangle_N \langle \hat{B} \rangle_N.$$

Performing a Fourier transform in space we have that $C_{AB}(k, t)$, defined by:

$$C_{AB}(k, t) = \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} C_{AB}(r, t)$$

is real and depends only on $k = |\vec{k}|$. From the fact that the right-hand side of (1.2) does not depend on \vec{r}' we have:

$$\begin{aligned} C_{AB}(k, t) &= \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} V \langle \hat{A}(\vec{r}', \Gamma(0)) \hat{B}(\vec{r} + \vec{r}', \Gamma(t)) \rangle_N = \\ &= \int d\vec{r} d\vec{r}' e^{-i\vec{k} \cdot \vec{r}} \langle \hat{A}(\vec{r}', \Gamma(0)) \hat{B}(\vec{r} + \vec{r}', \Gamma(t)) \rangle_N = \end{aligned}$$

$$= \int d\vec{r} d\vec{r}' e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \langle \hat{A}(\vec{r}', \Gamma(0)) \hat{B}(\vec{r}, \Gamma(t)) \rangle_N = \\ = \langle \hat{A}(-\vec{k}, \Gamma(0)) \hat{B}(\vec{k}, \Gamma(t)) \rangle_N,$$

where in the last integral the change of variable $\vec{r}' \rightarrow \vec{r}'$ and $\vec{r} + \vec{r}' \rightarrow \vec{r}$ has been made, and where

$$\hat{A}(\vec{k}, \Gamma(t)) = \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} \hat{A}(\vec{r}, \Gamma(t)).$$

One can also perform a Fourier transform in time to obtain:

$$C_{AB}(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} C_{AB}(k, t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle \hat{A}(-\vec{k}, \Gamma(0)) \hat{B}(\vec{k}, \Gamma(t)) \rangle_N.$$

If $\langle \hat{A}(-\vec{k}, \Gamma) \rangle_N$ and $\langle \hat{B}(\vec{k}, \Gamma) \rangle_N \neq 0$ it would be better to define $C_{AB}(k, \omega)$ by:

$$C_{AB}(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} [\langle \hat{A}(-\vec{k}, \Gamma(0)) \hat{B}(\vec{k}, \Gamma(t)) \rangle_N - \langle \hat{A}(-\vec{k}, \Gamma) \rangle_N \langle \hat{B}(\vec{k}, \Gamma) \rangle_N]$$

which for $\omega \neq 0$ is equivalent to the previous definition, but avoids a singularity at $\omega=0$. However, for the variables of interest to us here, we will always have that $\langle \hat{A}(\vec{k}, \Gamma) \rangle_N = 0$ for $k \neq 0$.

In the study of the equilibrium structure of fluids, the static (or equal time) correlation functions are of great importance. They are defined by the initial value of the (time-dependent) correlation functions just introduced:

$$C_{AB}(r) = C_{AB}(r, t) |_{t=0}$$

and

$$C_{AB}(k) = C_{AB}(k, t) |_{t=0}.$$

In most of the cases the dynamical variables have a definite parity with respect to time reversal; then we have the following properties: if \hat{A} and \hat{B} have opposite parities $C_{AB}(r, t)$ and $C_{AB}(k, t)$ are odd functions of time, and $C_{AB}(k, \omega)$ is purely imaginary and odd in ω . If \hat{A} and \hat{B} have the same parity (in particular if $\hat{A}=\hat{B}$) $C_{AB}(r, t)$ and $C_{AB}(k, t)$ are even in time,

while $C_{AB}(k, \omega)$ is real and even in ω . In this case, defining the Laplace transform by:

$$\tilde{C}_{AB}(k, z) = \int_0^{\infty} dt e^{-zt} C_{AB}(k, t)$$

with $\text{Re } z \geq 0$, then we have:

$$C_{AB}(k, \omega) = C_{AB}(k, -\omega) = \frac{1}{\pi} \text{Re} (\tilde{C}_{AB}(k, i\omega)) \quad (1.3)$$

1.1.3 Density-density correlation functions

Now I can introduce the correlation functions that are needed in my study of fluids, and in the next subsection I will explain their connection with light and neutron scattering experiments. It is useful to start with simple fluids and then to generalize to binary mixtures; this both for clarity and for later reference.

In a simple fluid the relevant dynamical variables are:

$$\hat{n}(\vec{r}, \Gamma(t)) = \frac{1}{\sqrt{N}} \sum_{p=1}^N \delta(\vec{r} - \vec{r}_p(t)) \quad (1.4)$$

(this definition differs from (1.1) by the factor of normalization), and its space Fourier transform:

$$\hat{n}(\vec{k}, \Gamma(t)) = \frac{1}{\sqrt{N}} \sum_{p=1}^N e^{-i\vec{k} \cdot \vec{r}_p(t)} \quad (1.5)$$

We define $\hat{\delta n}$ as the fluctuation of \hat{n} around its average value:

$$\hat{\delta n}(\vec{r}, \Gamma(t)) = \frac{1}{\sqrt{N}} \left[\sum_{p=1}^N \delta(\vec{r} - \vec{r}_p(t)) - n \right]$$

where $n = \langle \sum_{p=1}^N \delta(\vec{r} - \vec{r}_p(t)) \rangle_N$ is the number density of the fluid, so that

$\langle \hat{\delta n}(\vec{r}, \Gamma) \rangle_N = 0$. For $k \neq 0$ we have $\hat{\delta n}(\vec{k}, \Gamma(t)) = \hat{n}(\vec{k}, \Gamma(t))$, and besides $\langle \hat{n}(\vec{k}, \Gamma) \rangle_N = 0$.

We now define the density-density correlation function by:

$$F(k, t) = \langle \hat{n}^*(\vec{k}, \Gamma(0)) \hat{n}(\vec{k}, \Gamma(t)) \rangle_N \quad (1.6)$$

$\hat{n}(-\vec{k}, \Gamma) = \hat{n}^*(\vec{k}, \Gamma)$ called, in the literature, intermediate scattering function. $F(k, t)$ is proportional to the probability of having a density fluctuation, in Fourier space, of wavevector k , at time t , conditioned to the presence of a density fluctuation of the same wavelength at time zero. $F(k, t)$ is real and even in t . Its Fourier transform in time:

$$S(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} F(k, t) \quad (1.7)$$

is called the dynamic structure factor. It is real and even in ω ; besides it can be shown to be positive.

Important static correlation functions are the static structure factor, defined by:

$$S(k) = F(k, 0) = \frac{1}{N} \langle \left| \sum_{p=1}^N e^{-i\vec{k} \cdot \vec{r}_p} \right|^2 \rangle_N \quad (1.8)$$

(the second equality shows that $S(k)$ is positive definite) and the radial distribution function:

$$g(r) = V^2 \langle \delta(\vec{r}' - \vec{r}_1) \delta(\vec{r}' + \vec{r} - \vec{r}_2) \rangle_N. \quad (1.9)$$

Because of the homogeneity and isotropy of the fluid $g(r)$, which also is trivially positive definite as the expectation value of a positive function, does not depend on \vec{r}' , for fixed \vec{r} , and depends only on r . Besides, it does not depend on the choice of the pair of particles (in (1.9) particles 1 and 2), because of the symmetry of the hamiltonian with respect to the interchange of any two particles. It is proportional to the probability of finding any two different particles at a distance r between them. It is an easy matter to derive a relation between $S(k)$ and $g(r)$:

$$S(k) = 1 + n \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} (g(r) - 1) \quad (1.10)$$

In an ideal gas, where the particles are spatially uncorrelated, $g(r)=1$ and $S(k)=1$.

All the quantities above can be generalized to binary mixtures. Now we have a fluid in a volume V with N_1 particles of species 1 (of mass m_1) and N_2 particles of species 2 (of mass m_2), so that the partial number densities are $n_1=N_1/V$ and $n_2=N_2/V$; $N=N_1+N_2$. In the following, $\vec{r}_p^{(i)}$ and $\vec{v}_p^{(i)}$ will denote respectively the coordinate and the velocity of particle number p of species i .

We introduce the variables:

$$\hat{n}_i(\vec{r}, \Gamma(t)) = \frac{1}{\sqrt{N_i}} \sum_{p=1}^{N_i} \delta(\vec{r} - \vec{r}_p^{(i)}(t)) \quad (i=1,2) \quad (1.11)$$

and their Fourier transforms:

$$\hat{n}_i(\vec{k}, \Gamma(t)) = \frac{1}{\sqrt{N_i}} \sum_{p=1}^{N_i} e^{-i\vec{k} \cdot \vec{r}_p^{(i)}(t)} \quad (i=1,2) \quad (1.12)$$

Now we have four density-density correlation functions:

$$F_{ij}(k, t) = \langle \hat{n}_i^*(\vec{k}, \Gamma(0)) \hat{n}_j(\vec{k}, \Gamma(t)) \rangle_N \quad (i, j=1,2) \quad (1.13)$$

the partial intermediate scattering functions. The $F_{ij}(k, t)$ are all real, even in t and $F_{12}(k, t) = F_{21}(k, t)$. Their Fourier transforms in time, the partial dynamic structure factors:

$$S_{ij}(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} F_{ij}(k, t) \quad (i, j=1,2) \quad (1.14)$$

are real, even in ω , with $S_{12}(k, \omega) = S_{21}(k, \omega)$ and with $S_{11}(k, \omega)$ and $S_{22}(k, \omega)$ positive. From (1.3) we have:

$$S_{ij}(k, \omega) = \frac{1}{\pi} \text{Re } \tilde{S}_{ij}(k, z)$$

where $\tilde{S}_{ij}(k, z)$ is the Laplace transform of $F_{ij}(k, t)$:

$$\tilde{S}_{ij}(k, z) = \int_0^{\infty} dt e^{-zt} F_{ij}(k, t)$$

The static correlation functions analogous to (1.6) and (1.7) are the partial static structure factors:

$$S_{ij}(k) = F_{ij}(k,0) = \frac{1}{\sqrt{N_i N_j}} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \langle e^{i\vec{k} \cdot \vec{r}_p^{(i)}} e^{-i\vec{k} \cdot \vec{r}_q^{(j)}} \rangle_N \quad (i,j=1,2) \quad (1.15)$$

and the partial radial distribution functions, defined by:

$$g_{ij}(r) = V^2 \langle \delta(\vec{r}' - \vec{r}_1^{(i)}) \delta(\vec{r}' + \vec{r} - \vec{r}_2^{(j)}) \rangle_N \quad (i,j=1,2) \quad (1.16)$$

which, like $g(r)$ for a simple fluid (cf. (1.9)), depend only on r . We have the properties that $S_{12}(k)=S_{21}(k)$, $g_{12}(r)=g_{21}(r)$ and that all the $g_{ij}(r)$, $S_{11}(k)$ and $S_{22}(k)$ are positive definite. Besides we have the Schwarz inequality:

$$S_{11}(k)S_{22}(k) - S_{12}^2(k) \geq 0. \quad (1.17)$$

These properties of the $S_{ij}(k)$ will be needed in the next chapter in the construction of our kinetic theory. The expression analogous to (1.10) is:

$$S_{ij}(k) = \delta_{ij} + \sqrt{n_i n_j} \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} (g_{ij}(r) - 1) \quad (1.18)$$

1.1.4 Light and neutron scattering

Now I can explain the connection between light and neutron scattering experiments and the correlation functions. As in the previous subsection, I will begin with simple fluids and then I will generalize to binary mixtures. The detailed calculations can be found in textbooks^{1,2)}.

I. Light scattering

When we perform light scattering experiments incident light (generally light from a laser that has passed through a polarizer) with wavevector \vec{k}_i and frequency ω_i is scattered by the fluid. The scattered light is a superposition of waves with different wavevectors \vec{k}_f and frequencies ω_f . In

each wave the frequency shift is $\omega = \omega_f - \omega_i$ and the wavenumber transfer is $\vec{k} = \vec{k}_f - \vec{k}_i$, so that $\hbar\omega$ ($\hbar\vec{k}$) is the energy gained by (the momentum transferred to) a photon. In the experiments one looks for the intensity of the scattered light at a given frequency and at a given scattering angle, a quantity which defines the differential scattering cross section: $d^2\sigma/d\omega d\Omega$, where $d\Omega$ is an element of solid angle. One can prove that¹⁾:

$$\frac{d^2\sigma}{d\omega d\Omega} \propto \int_{-\infty}^{+\infty} dt e^{i\omega t} \left\langle \sum_{p=1}^N \alpha_p e^{i\vec{k} \cdot \vec{r}_p(0)} \sum_{q=1}^N \alpha_q e^{-i\vec{k} \cdot \vec{r}_q(t)} \right\rangle_N \quad (1.19)$$

In this formula the correlation function on the right-hand side contains the vector \vec{k} (but it depends only on $k = |\vec{k}|$) and the polarizabilities α_p of the particles of the fluid. On the left-hand side the dependence on k is through the solid angle Ω and ω (or $\omega_f = \omega_i + \omega$): if θ is the scattering angle and ω_f

the scattered frequency, then $k_i = \omega_i/c$, $k_f = \omega_f/c$, and $k = \sqrt{k_i^2 + k_f^2 - 2k_i k_f \cos\theta} = \sqrt{\omega_i^2 + \omega_f^2 - 2\omega_i \omega_f \cos\theta}/c$. But the frequency shift ω , which is due to the translational motion of the particles, is much smaller than ω_i , where typically $\omega_i \sim 10^{15} \text{ s}^{-1}$ (and $k_i \sim 10^5 \text{ cm}^{-1}$). Therefore $\omega_f \approx \omega_i$, so that $k_f \approx k_i$ and $k \approx 2k_i \sin\theta/2$. As a consequence, in general in actual experiments the scattering angle is taken to define uniquely k . In (1.19) I have used a proportionality sign because I have neglected the factors in front of the integral, which are not of interest here. In a simple fluid all the polarizabilities α_p are equal to a common value α , therefore from (1.19) and from the definitions (1.5), (1.6) and (1.7) we have:

$$\frac{d^2\sigma}{d\omega d\Omega} \propto \alpha^2 S(k, \omega) \quad (1.20)$$

In a binary mixture there are two different polarizabilities, α_1 and α_2 , corresponding respectively to the two components. Therefore (1.19) can be rewritten as:

$$\frac{d^2\sigma}{d\omega d\Omega} \propto \int_{-\infty}^{+\infty} dt e^{i\omega t} \left\langle \sum_{i=1}^2 \alpha_i \sum_{p=1}^{N_i} e^{i\vec{k} \cdot \vec{r}_p^{(i)}(0)} \sum_{j=1}^2 \alpha_j \sum_{q=1}^{N_j} e^{-i\vec{k} \cdot \vec{r}_q^{(j)}(t)} \right\rangle_N$$

and from (1.12), (1.13) and (1.14) we have:

$$\frac{d^2\sigma}{d\omega d\Omega} \propto x_1 \alpha_1^2 S_{11}(k, \omega) + x_2 \alpha_2^2 S_{22}(k, \omega) + 2\sqrt{x_1 x_2} \alpha_1 \alpha_2 S_{12}(k, \omega) \quad (1.21)$$

where $x_i = n_i / (n_1 + n_2)$ is the relative number concentration of species i .

II. Neutron scattering

In neutron scattering experiments a beam of neutrons with momentum \vec{p}_i and energy ϵ_i , described by plane waves of wavevector $\vec{k}_i = \vec{p}_i / \hbar$ and frequency $\omega_i = \epsilon_i / \hbar = \hbar k_i^2 / 2m_n$ (m_n is the neutron mass) is scattered by the fluid at different angles, with different wavevectors \vec{k}_f and energies ω_f . To compute the probability for a neutron to be scattered with a given energy and at a given angle the golden rule formula of perturbation theory is used, and the interaction between the neutrons and the particles of the fluid is described by the Fermi pseudo-potential. An expression completely analogous to light scattering is found for the differential scattering cross section. For simple fluids we have²⁾:

$$\frac{d^2\sigma}{d\omega d\Omega} \propto b^2 S(k, \omega) \quad (1.22)$$

where now b is the scattering length of a particle in the Fermi potential, and, like in light scattering, $k = |\vec{k}_f - \vec{k}_i|$ and $\omega = \omega_f - \omega_i$, and on the left-hand side the dependence on k is through Ω and ω . The orders of magnitude of ω_i and k_i are different from those in light scattering. Neutrons used in experiments are thermalized, and thus $\omega_i \sim 10^{13} \text{ s}^{-1}$ and $k_i \sim 10^8 \text{ cm}^{-1}$. Therefore it is clear that light and neutron scattering experiments probe fluid

dynamics at different wavelengths and energies. Now the frequency shift ω is comparable with ω_i [4], and, contrary to light scattering, the dependence of k on ω and the scattering angle θ has to be considered more carefully. A straightforward calculation yields:

$$k = \frac{\sqrt{2m\omega_i}}{\hbar} \left[2 - \frac{\omega}{\omega_i} - 2\sqrt{1 - \frac{\omega}{\omega_i} \cos \theta} \right]^{1/2}.$$

With respect to light scattering, there is an additional difference when the fluid is made of particles with non zero spin and/or different isotopes (where it is assumed that different isotopes of a given atom are dynamically equivalent; this is true, to a very good approximation, for the isotopes of heavy atoms). In this case the scattering length depends on the spin state of the compound system composed by the neutron and the particle by which it is scattered, and on the isotopic species. Then a different result is obtained for the differential scattering cross section. Before giving its expression I have to introduce the so called self correlation functions, which describe the correlations in the motion of a tagged particle in the fluid. For the self intermediate scattering function we have, if the tagged particle is particle 1 in a simple fluid:

$$F^S(k, t) = \langle e^{i\vec{k} \cdot \vec{r}_1(0)} e^{-i\vec{k} \cdot \vec{r}_1(t)} \rangle_N \quad (1.23)$$

This result does not depend on the choice of the tagged particle, for an analogous reason as for (1.9), namely the symmetry of the Liouville operator as well as the hamiltonian with respect to the interchange of any two particles. The Fourier transform in time of (1.23) is the self dynamic structure factor:

$$S^S(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} F^S(k, t). \quad (1.24)$$

Besides one has to introduce an average of the scattering length over the different spin states and the different isotopes. Denoting this average by $\langle \cdot \rangle_q$, we have that $d^2\sigma/d\omega d\Omega$ is divided in two parts:

$$\frac{d^2\sigma}{d\omega d\Omega} = \left(\frac{d^2\sigma}{d\omega d\Omega} \right)_{\text{coherent}} + \left(\frac{d^2\sigma}{d\omega d\Omega} \right)_{\text{incoherent}} \quad (1.25)$$

where:

$$\left(\frac{d^2\sigma}{d\omega d\Omega} \right)_{\text{coherent}} \propto \langle b \rangle_q^2 S(k, \omega) \quad (1.26)$$

and

$$\left(\frac{d^2\sigma}{d\omega d\Omega} \right)_{\text{incoherent}} \propto (\langle b^2 \rangle_q - \langle b \rangle_q^2) S^S(k, \omega) \quad (1.27)$$

The second part, (1.27), is called incoherent scattering because it is proportional to the self dynamic structure factor, which does not contain correlation between different particles. For a mono-isotopic fluid and a scattering length independent of the spin state $\langle b^2 \rangle_q = \langle b \rangle_q^2 = b^2$, the incoherent part is absent, and we obtain (1.22), where $d^2\sigma/d\omega d\Omega$ gives directly $S(k, \omega)$. When there is also incoherent scattering it is possible to determine both $S(k, \omega)$ and $S^S(k, \omega)$; this could be accomplished either by using polarized neutrons or by varying the isotopic composition. This is because in these cases one changes the values of $\langle b \rangle_q^2$ and $\langle b^2 \rangle_q$; therefore, comparing sets of data for $d^2\sigma/d\omega d\Omega$ obtained, for example, with different isotopic compositions, one can extract both $S(k, \omega)$ and $S^S(k, \omega)$.

In binary mixtures the generalization of (1.22) is:

$$\frac{d^2\sigma}{d\omega d\Omega} \propto x_1 b_1^2 S_{11}(k, \omega) + x_2 b_2^2 S_{22}(k, \omega) + 2\sqrt{x_1 x_2} b_1 b_2 S_{12}(k, \omega) \quad (1.28)$$

where b_i is the scattering length of species i . When the scattering lengths depend on the spin state (or when there are different isotopes) then we have an expression like (1.25), where now:

$$\left(\frac{d^2\sigma}{d\omega d\Omega}\right)_{\text{coherent}} \propto x_1 \langle b_1 \rangle_q^2 S_{11}(k, \omega) + x_2 \langle b_2 \rangle_q^2 S_{22}(k, \omega) + 2\sqrt{x_1 x_2} \langle b_1 \rangle_q \langle b_2 \rangle_q S_{12}(k, \omega) \quad (1.29)$$

and

$$\left(\frac{d^2\sigma}{d\omega d\Omega}\right)_{\text{incoherent}} \propto x_1 (\langle b_1^2 \rangle_q - \langle b_1 \rangle_q^2) S_{11}^s(k, \omega) + x_2 (\langle b_2^2 \rangle_q - \langle b_2 \rangle_q^2) S_{22}^s(k, \omega) \quad (1.30)$$

where the self dynamic structure factors are given by:

$$S_{ii}^s(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} F_{ii}^s(k, t) \quad (i=1,2) \quad (1.31)$$

and the self intermediate scattering functions by:

$$F_{ii}^s(k, t) = \langle e^{i\vec{k} \cdot \vec{r}_1^{(i)}(0)} e^{-i\vec{k} \cdot \vec{r}_1^{(i)}(t)} \rangle_N \quad (i=1,2) \quad (1.32)$$

which, analogously to simple fluids, do not depend on the choice of the tagged particle of a given species. So we see that for binary mixtures the situation is much more complicated, already for the case when there is no incoherent scattering, because the measurements give informations only on the expression (1.28) and not on the $S_{ij}(k, \omega)$ separately (of course this is true also in light scattering). Here I will be concerned with neutron scattering by binary noble gas fluid mixtures. For noble gases, with the exception of Argon, incoherent scattering can be neglected, because the scattering lengths for different isotopes are very similar. However, the two isotopes of Argon, ^{40}Ar and ^{36}Ar , have very different scattering lengths, because ^{36}Ar is an exceptionally strong neutron scatterer. Since the two isotopes can be separated, it is possible to perform experiments with mono-isotope Argon, so that incoherent scattering is absent.

Another important point in neutron scattering is that, contrary to light scattering, it is possible in principle to measure the $S_{ij}(k, \omega)$ separately, using different isotopes in different experiments.

1.1.5 Hydrodynamics

To make theoretical predictions to compare with experiments one needs a method to compute the partial dynamic structure factors. In the hydrodynamic limit, that is in the region of small k and ω , small compared respectively to the inverse of any typical microscopic length and to the inverse of any microscopic relaxation time, the motion of the fluid is governed by the hydrodynamic equations. They describe the evolution in time of the thermodynamic variables plus the local velocity of the fluid, making use of linear phenomenological laws that relate the momentum and the energy fluxes to the gradient of the local velocity and the local temperature, respectively. In the case of binary mixtures, among the thermodynamic variables there is the relative concentration of one of the two components; then the phenomenological laws contain also the gradient of the local concentration. Transport coefficients appear in the hydrodynamic equations, which can not be computed in the framework of thermodynamics and hydrodynamics; their values must be given experimentally or be computed using kinetic theories. In the hydrodynamic description use is made of the local equilibrium assumption, that means that at each point in the fluid the thermodynamic variables are related by the same thermodynamic relations as in total equilibrium. This is the reason why hydrodynamics is good only when k and ω are small in the above sense. Linearizing the hydrodynamic equation around total equilibrium (the linearization is harmless in the study of microscopic fluctuations) one can get formulas for the dynamic structure factors for small k and ω .

When k and ω are not small in the sense mentioned above, and hydrodynamics ceases to be a good theory for the study of the dynamics of the fluid, and a more microscopic point of view has to be used. Kinetic theory provides a possibility to do that.

1.2 Kinetic theories

In this section, which gives a short summary of the developments of kinetic theories, I will restrict myself to simple fluids, to avoid unnecessary complications. All the definitions can be generalized to binary mixtures without change of the basic concepts.

1.2.1 The Boltzmann and Enskog equations

The first milestone in kinetic theories is, without any doubt, the celebrated Boltzmann equation. For a simple fluid, we define the one-particle distribution function $f(\vec{r}, \vec{v}, t)$ in such a way that $f(\vec{r}, \vec{v}, t) \Delta \vec{r} \Delta \vec{v}$ is the average number of particles that lie at time t within a volume element $\Delta \vec{r}$ around point \vec{r} and have a velocity in the element $\Delta \vec{v}$ around \vec{v} . Making two basic assumptions, Boltzmann was able to derive a closed equation which describes the time evolution of $f(\vec{r}, \vec{v}, t)$. The first assumption is that in the dynamics of the particles only binary collisions are taken into account, which are considered local in space and time. The second assumption, called molecular-chaos assumption, states that the average number of pair of molecules in the element $\Delta \vec{r}$ around \vec{r} and with respective velocities in the

element $\Delta\vec{v}$ around \vec{v} and $\Delta\vec{v}'$ around \vec{v}' , which can participate in a collision at time t , is given by:

$$f(\vec{r}, \vec{v}, t) \Delta\vec{r} \Delta\vec{v} f(\vec{r}, \vec{v}', t) \Delta\vec{r} \Delta\vec{v}' \quad (1.33)$$

The first assumption can be justified in dilute gases, where the range of the intermolecular interaction is much smaller than the average distance between molecules. Then it follows that it is very unlikely to have more than two molecules in their mutual range of interaction. The second assumption means that the velocities of the two colliding molecules are uncorrelated. This also can be justified in dilute gases; two molecules that are going to collide will come in general from different regions of space and have collided before the collision with many other particles, so that it is reasonable to assume that their velocities are completely uncorrelated. Following these assumptions the Boltzmann equation for a fluid in the absence of an external field is derived to be³⁾:

$$\frac{\partial}{\partial t} f(\vec{r}, \vec{v}, t) + \vec{v} \cdot \frac{\partial}{\partial \vec{r}} f(\vec{r}, \vec{v}, t) = \int d\vec{v}_1 \int d\Omega \sigma(\theta, |\vec{v} - \vec{v}_1|) |\vec{v} - \vec{v}_1| \left[f(\vec{r}, \vec{v}', t) f(\vec{r}, \vec{v}'_1, t) - f(\vec{r}, \vec{v}, t) f(\vec{r}, \vec{v}_1, t) \right] \quad (1.34)$$

In this equation \vec{v}' and \vec{v}'_1 are the final velocities of a binary collision of two particles with initial velocities \vec{v} and \vec{v}_1 , and they depend on \vec{v} , \vec{v}_1 and on the scattering angles θ , ϕ , defined as the angles, in polar coordinates with the polar axis parallel to $\vec{v}_1 - \vec{v}$, which give the direction of $\vec{v}'_1 - \vec{v}'$; $\Omega = (\theta, \phi)$ and $\sigma(\theta, |\vec{v} - \vec{v}_1|)$ is the differential collision cross section which depends on the modulus of the relative velocity, on the scattering angle θ , and, of course, on the assumed intermolecular potential. Perhaps the most important point concerning the Boltzmann equation is the existence of the so called H theorem, which proves that, for any given initial distribution function $f(\vec{r}, \vec{v}, 0)$, the solution of (1.34), making very general and

reasonable assumptions about the shape of the container⁴⁾, will approach the absolute equilibrium Maxwell distribution function:

$$f(\vec{r}, \vec{v}, t) \rightarrow f_M(\vec{v}) = n \left(\frac{\beta m}{2\pi} \right)^{3/2} e^{-\frac{\beta m v^2}{2}} \quad (1.35)$$

where n is the uniform density of the fluid and the value of the temperature T in $\beta = 1/k_B T$ is defined by the average kinetic energy of the particles of the fluid:

$$\frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{n} \int d\vec{v} v^2 f_M(\vec{v}) \quad (1.36)$$

The problem of finding a solution of (1.34) is a field in its own right, which is not of interest here. However, one important point must be mentioned. Following a solution procedure, due to Chapman and Enskog, in which $f(\vec{r}, \vec{v}, t)$ is expressed as a sum of an infinite series, it is possible to derive hydrodynamic equations with transport coefficients given explicitly as functions of the intermolecular potential³⁾.

From the basic assumptions it follows that the Boltzmann equation is valid only in the limit of dilute gases. It was Enskog who proposed a kinetic theory for dense systems, restricted to fluids consisting of particles interacting through a hard sphere potential. If r is the distance between two particles, the hard sphere potential is such that $U(r)$ is equal to zero for r larger than a constant σ , the diameter of the hard spheres, and $U(r)$ is infinite for $r \leq \sigma$. With this interaction the particles can be visualized as spheres of diameter σ ; when two spheres come at contact, so that the distance between their centres is σ , they bounce rigidly off each other. Therefore the collision is instantaneous, and in a fluid of hard spheres there is no approximation in considering the collisions purely binary, because the probability for more than two molecules to interact at

the same instant is zero. This is the main characteristic of hard sphere fluids, together with the fact that, at the moment of a binary collision, the velocity of the two particles changes discontinuously (this fact is important for the determination of the proper time evolution operator for hard spheres, which replaces the Liouville operator for smooth potentials, and that will be introduced later).

Also the derivation of the Enskog kinetic equation makes use of the molecular chaos assumption. Of course, also for hard spheres this assumption is not expected to be fulfilled when the fluid is dense, because two colliding molecules could be correlated if they collided before with each other or with the same molecule. Nevertheless, comparison with computer simulations of hard sphere systems shows fairly good agreement ⁵⁾.

There are two changes in the Enskog equation, with respect to the Boltzmann equation. The first one is to increase the frequency of binary collisions by a factor which depends on the local density of the fluid; this can be understood from the fact that the molecules occupy a finite portion of the total volume. This decreases the volume in which the center of any given molecule can lie, and therefore increases the probability of a collision. The second change is that one takes into account that the centers of two colliding spheres lie at a distance σ . Then the Enskog equation is ³⁾:

$$\frac{\partial}{\partial t} f(\vec{r}, \vec{v}, t) + \vec{v} \cdot \frac{\partial}{\partial \vec{r}} f(\vec{r}, \vec{v}, t) = \sigma^2 \int d\vec{v}_1 \int d\hat{\sigma} [(\vec{v}_1 - \vec{v}) \cdot \hat{\sigma}] \theta((\vec{v}_1 - \vec{v}) \cdot \hat{\sigma}) \times \quad (1.37)$$

$$\left\{ \chi \left[n(\vec{r} + \frac{\sigma \hat{\sigma}}{2}, t) \right] f(\vec{r}, \vec{v}', t) f(\vec{r} + \sigma \hat{\sigma}, \vec{v}'_1, t) - \chi \left[n(\vec{r} - \frac{\sigma \hat{\sigma}}{2}, t) \right] f(\vec{r}, \vec{v}, t) f(\vec{r} - \sigma \hat{\sigma}, \vec{v}_1, t) \right\}$$

$\hat{\sigma}$ is a unit vector characterizing the geometry of the binary collision, and the final velocities \vec{v}' and \vec{v}'_1 are expressed in terms of \vec{v} , \vec{v}_1 and $\hat{\sigma}$ by:

$$\vec{v}' = \vec{v} + [(\vec{v}_1 - \vec{v}) \cdot \hat{\sigma}] \hat{\sigma}$$

$$\vec{v}'_1 = \vec{v}_1 - [(\vec{v}_1 - \vec{v}) \cdot \hat{\sigma}] \hat{\sigma}$$

The factor χ determines the increase in the frequency of binary collisions; it has been chosen equal to the equilibrium radial distribution function at contact, $\chi=g(\sigma)$, evaluated, as shown in (1.37), for the density at the point of contact.

An important consequence of (1.37), absent in the Boltzmann equation, is the instantaneous transfer of molecular properties (like momentum and energy) over a finite distance; this comes from the fact that in (1.37) the f 's are evaluated at different points in space. Finally, it should be mentioned that also from the Enskog equation one can compute explicit expressions for the transport coefficients of a hard sphere fluid.

1.2.2 Linearized equations and correlation functions

Both equations (1.34) and (1.37) can be linearized assuming that the distribution function $f(\vec{r}, \vec{v}, t)$ is close to its absolute equilibrium value (1.35). Then one obtains linear equations governing the evolution of the fluctuation of $f(\vec{r}, \vec{v}, t)$ around $f_M(\vec{v})$. It is these linear equations that can also be used to study the time correlation functions. One proceeds as follows.

Defining first $\Delta f(\vec{r}, \vec{v}, t)$ by $f(\vec{r}, \vec{v}, t) = f_M(\vec{v}) + \Delta f(\vec{r}, \vec{v}, t)$, and linearizing the Boltzmann equation (1.34) one gets an equation for $\Delta f(\vec{r}, \vec{v}, t)$:

$$\frac{\partial}{\partial t} \Delta f(\vec{r}, \vec{v}, t) + \vec{v} \cdot \frac{\partial}{\partial \vec{r}} \Delta f(\vec{r}, \vec{v}, t) = \Lambda_B \Delta f(\vec{r}, \vec{v}, t) \quad (1.38)$$

where Λ_B is a linear integral operator which acts only on the \vec{v} dependence of Δf . This equation describes the approach to zero of $\Delta f(\vec{r}, \vec{v}, t)$. $\Delta f(\vec{r}, \vec{v}, t)$ is an external perturbation of the fluid from its equilibrium state; therefore it is a macroscopic perturbation. Next one uses a general

assumption of statistical mechanics, the Onsager regression hypothesis, according to which, on the average, the decay of microscopic spontaneous fluctuations, or of the correlations between fluctuations, follows the same linearized equation, in this case (1.38), as a small external disturbance. This result could also be reached, somewhat more satisfactorily from the mathematical point of view, using linear response theory⁶⁾.

To introduce the proper correlation function which follows (1.38) I first introduce the dynamical variable:

$$\hat{f}(\vec{r}, \vec{v}, \Gamma(t)) = \sum_{p=1}^N \delta(\vec{r} - \vec{r}_p(t)) \delta(\vec{v} - \vec{v}_p(t)) \quad (1.39)$$

If the average is taken over the canonical ensemble [5] one obtains the equilibrium value:

$$\langle \hat{f}(\vec{r}, \vec{v}, \Gamma) \rangle_N = f_M(\vec{v}) \quad (1.40)$$

Then, defining the fluctuation as the dynamical variable:

$$\delta \hat{f}(\vec{r}, \vec{v}, \Gamma(t)) = \hat{f}(\vec{r}, \vec{v}, \Gamma(t)) - \langle \hat{f}(\vec{r}, \vec{v}, \Gamma) \rangle_N \quad (1.41)$$

we have that (1.38) is satisfied if $\delta f(\vec{r}, \vec{v}, t)$ is replaced by the following correlation function:

$$C(|\vec{r} - \vec{r}_1|, \vec{v}, \vec{v}_1, t) = V \langle \delta \hat{f}(\vec{r}_1, \vec{v}_1, \Gamma(0)) \delta \hat{f}(\vec{r}, \vec{v}, \Gamma(t)) \rangle_N \quad (1.42)$$

(where the factor V , the volume of the fluid, has been used for convenience), i. e.:

$$\frac{\partial}{\partial t} C(|\vec{r} - \vec{r}_1|, \vec{v}, \vec{v}_1, t) + \vec{v} \cdot \frac{\partial}{\partial \vec{r}} C(|\vec{r} - \vec{r}_1|, \vec{v}, \vec{v}_1, t) = \Lambda_B C(|\vec{r} - \vec{r}_1|, \vec{v}, \vec{v}_1, t) \quad (1.43)$$

Then one defines the spatial Fourier transform of (1.42):

$$\begin{aligned} C(k, \vec{v}, \vec{v}_1, t) &= \int d(\vec{r} - \vec{r}_1) e^{-i\vec{k} \cdot (\vec{r} - \vec{r}_1)} C(|\vec{r} - \vec{r}_1|, \vec{v}, \vec{v}_1, t) = \\ &= \int d(\vec{r} - \vec{r}_1) d\vec{r}_1 e^{-i\vec{k} \cdot (\vec{r} - \vec{r}_1)} \langle \delta \hat{f}(\vec{r}_1, \vec{v}_1, \Gamma(0)) \delta \hat{f}(\vec{r}, \vec{v}, \Gamma(t)) \rangle_N = \\ &= \langle \delta \hat{f}^*(\vec{k}, \vec{v}_1, \Gamma(0)) \delta \hat{f}(\vec{k}, \vec{v}, \Gamma(t)) \rangle_N \end{aligned} \quad (1.44)$$

(which depends only on $k=|\vec{k}|$ because of the isotropy at equilibrium) where, from (1.39) and for $k \neq 0$:

$$\hat{\delta f}(\vec{k}, \vec{v}, \Gamma(t)) = \sum_{p=1}^N \delta(\vec{v} - \vec{v}_p(t)) e^{-i\vec{k} \cdot \vec{r}_p(t)}$$

The equation for $C(k, \vec{v}, \vec{v}_1, t)$ is then obtained from the Fourier transform of (1.43):

$$\frac{\partial}{\partial t} C(k, \vec{v}, \vec{v}_1, t) + i\vec{k} \cdot \vec{v} C(k, \vec{v}, \vec{v}_1, t) = \Lambda_B C(k, \vec{v}, \vec{v}_1, t) \quad (1.45)$$

From a solution of this equation the intermediate scattering function $F(k, t)$ can be obtained (see (1.4) and (1.6)):

$$F(k, t) = \frac{1}{N} \int d\vec{v} d\vec{v}_1 C(k, \vec{v}, \vec{v}_1, t) \quad (1.46)$$

1.2.3 Later developments

Most of the recent theoretical work has been aimed at the derivation of kinetic equations for the correlation functions, these being the quantities of greatest interest for the reasons explained in section 1.1. I will mention only what is of interest here.

In this thesis I have used the hard sphere model for the interaction between the molecules, because this is the only model for which a kinetic equation is available for mixtures both at low and high densities. Therefore I will briefly outline the latest developments concerning the kinetic theory of hard spheres.

In 1969 Ernst et al.⁷⁾ derived the time evolution operator that describes the dynamics of a hard sphere fluid. Its expression will be given in the next chapter. Later, Konijnendijk and van Leeuwen⁸⁾, starting from

this operator and making a binary collision approximation, have derived a linear kinetic equation for the correlation function (1.44):

$$\frac{\partial}{\partial t} C(k, \vec{v}, \vec{v}_1, t) = -i\vec{k} \cdot \vec{v} C(k, \vec{v}, \vec{v}_1, t) + B(\vec{k}) C(k, \vec{v}, \vec{v}_1, t) \quad (1.47)$$

where $B(\vec{k})$ is a linear integral operator, depending parametrically on \vec{k} and acting on the \vec{v} dependence of $C(k, \vec{v}, \vec{v}_1, t)$. They also showed that for short times this equation is exact at all densities [6].

Successively, van Beijeren and Ernst⁹⁾ derived a modified Enskog equation. The difference from (1.37) is that the factor χ is no more the equilibrium radial distribution function, but it is the exact radial distribution function in a non uniform fluid, which is a functional of the density of the fluid at all points. This exact radial distribution function is then evaluated at the point of contact. Their motivation was that in the case of mixtures (1.37) led to inconsistencies with irreversible thermodynamics. They also showed that the linearized version of their equation leads to an equation identical to (1.47).

1.3 Outline of later chapters

In this section I summarize the contents of the following chapters.

In Chapter 2 I will derive the kinetic operator which will be used for the calculations. I will first derive the operator for simple fluids, and then its extension to binary mixtures. The fundamental quantity in my analysis will not be the correlation function $C(k, \vec{v}, \vec{v}_1, t)$ of (1.47). This will be replaced by an infinite set of correlation functions, obtained by integrating $C(k, \vec{v}, \vec{v}_1, t)$ over the velocities, analogously to (1.46). The reason for such a choice is explained in the first section of the next

chapter. There I discuss a method¹⁰⁾ for deriving our kinetic operators (both for simple fluids and for mixtures) which is relatively fast, and shows clearly that the corresponding kinetic equations are exact, for short times, at all densities. One requires that the kinetic equation reproduces exactly the values at time zero and the first time derivatives, at time zero, of the set of correlation functions, that will be introduced in the next chapter, where also the details of the procedure will be given.

Chapter 3 is technical. It contains some details of the actual computation I have carried out to obtain numerical results for the density-density correlation functions.

In Chapter 4 I will show these results. They concern the application of our kinetic theory both to dilute (gaseous) mixtures and to dense mixtures. The main subject of the results is the study of the characteristic behavior of binary mixtures where the atomic masses of the molecules of the two components are very different (disparate-mass binary mixtures). I will also explain how the predictions presented can be tested in scattering experiments.

As will be explained in the following chapter, in the description of the dynamics of the fluid through the density-density correlation functions, one can introduce the modes, which can be thought of as the different channels by which the correlations decay in time. Some modes are propagating, in the sense that they describe propagating, and damped, processes. Others are not propagating, and describe diffusive, purely damped processes.

The results concern the appearance of a fast propagating mode, in disparate-mass binary mixtures, in a vast range of densities, from dilute

gas mixtures to rather high (liquid) densities. This fast mode appears beyond the hydrodynamic regime. One can call this mode fast sound, because, like ordinary sound, it propagates, but it is faster. The most important point is that the fast sound is associated with the dynamics of the light component only. In Chapter IV I will explain how this phenomenon could be observed in light and neutron scattering experiments.

In Chapter 5 I will give the conclusions of this work.

Notes

[1] At equal density and temperature, the lighter the atoms of the fluid are, the larger the typical frequencies associated with the dynamics are.

[2] To be precise, the variables of the phase space of a system are the coordinates and the momenta. But using cartesian coordinates the relation between velocities and momenta is trivial.

[3] I refer here only to short range intermolecular interactions; the actual computation will be in fact performed for a hard sphere interaction (see text below).

[4] In the interaction with a neutron, the recoil of a nucleus can in general not be neglected.

[5] In a hard sphere system by definition the energy is only kinetic. The meaning of the canonical average $\langle \dots \rangle_N = (1/Z) \int d\Gamma e^{-\beta H(\Gamma)} (\dots)$ is that in configuration space $(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ one has to exclude all the configurations in which the centers of at least one pair of particles are at a distance smaller than the diameter. This could formally be achieved

writing $e^{-\beta H(\Gamma)} = W e^{-\beta K(\Gamma)}$, where $K(\Gamma)$ is the kinetic energy, and W a factor equal to one for the allowed configurations, and equal to zero for the forbidden configurations.

[6] Perhaps it is necessary to make the following clarification. The fact that in hard spheres the collisions always involve only two particles does not mean that a binary collision description of the dynamics is exact. Binary collision approximation means something else; it is an approximation (for hard spheres as well as for smooth potentials) in which any two given particles collide at most once. Therefore, for example, an event in which particle 1 collides successively with particle 2, particle 3 and again with particle 2, is neglected. From this it is easy to understand why the approximation is exact at short times for all densities, and improves, at finite times, decreasing the density.

Kinetic theory of correlation functions

In this chapter I show how the correlation functions of interest, namely the partial dynamic structure factors $S_{ij}(k, \omega)$ are computed in our kinetic theory. In the first two sections I will treat simple fluids: in the first one I will derive the kinetic equation, while in the second I will describe the actual method of computation, with the kind of approximation involved. In the third section the kinetic equation and the method of computation will be generalized to binary mixtures. In the fourth section I will show how the kinetic theory of binary mixtures reduces properly to that of simple fluids when the two components become equal; an interesting result of this limiting procedure will be given.

2.1 Kinetic equation

The time evolution operator for a simple hard sphere fluid, called the pseudo-Liouville operator, is the following:

$$L = \sum_{p=1}^N \vec{v}_p \cdot \frac{\partial}{\partial \vec{r}_p} + \sum_{p=1}^N \sum_{q>p} T_{pq} = \sum_{p=1}^N \vec{v}_p \cdot \frac{\partial}{\partial \vec{r}_p} + \frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N T_{pq} \quad (2.1)$$

The first term on the right-hand side of (2.1) describes the free streaming of the particles, while T_{pq} describes a binary collision between particle p and particle q . In the second equality, which follows from the fact that $T_{pq} = T_{qp}$, as will be shown below, I make the convention that $T_{pp} = 0$ (i. e., a particle does not collide with itself). T_{pq} is given by:

$$T_{pq} = \sigma^2 \int d\hat{\sigma} \delta(\vec{r}_{pq} + \vec{\sigma}) \theta(\vec{v}_{pq} \cdot \hat{\sigma}) |\vec{v}_{pq} \cdot \hat{\sigma}| [b_{pq}(\hat{\sigma}) - 1] \quad (2.2)$$

where σ is the hard sphere diameter, $\hat{\sigma}$ is a unit vector, $\vec{\sigma} = \sigma \hat{\sigma}$, $\theta(x)$ is the Heaviside step function, $\vec{r}_{pq} = \vec{r}_p - \vec{r}_q$, $\vec{v}_{pq} = \vec{v}_p - \vec{v}_q$, and $b_{pq}(\hat{\sigma})$ transforms the precollisional velocities into the postcollisional velocities:

$$\begin{aligned} b_{pq}(\hat{\sigma}) \vec{v}_p &= \vec{v}_p' = \vec{v}_p - (\vec{v}_{pq} \cdot \hat{\sigma}) \hat{\sigma} \\ b_{pq}(\hat{\sigma}) \vec{v}_q &= \vec{v}_q' = \vec{v}_q + (\vec{v}_{pq} \cdot \hat{\sigma}) \hat{\sigma} \end{aligned} \quad (2.3)$$

By definition, the substitution operator b_{pq} , acting on any function of \vec{v}_p and/or \vec{v}_q , transforms these velocities into those given by (2.3). The δ function and the step function in T_{pq} account respectively for the facts that the two particles collide only when they are at a distance σ and when they move towards one another. From (2.3) it is easily seen that $b_{pq}(\hat{\sigma}) = b_{pq}(-\hat{\sigma}) = b_{qp}(\hat{\sigma})$, and therefore, from (2.2) it follows immediately (with the change of variable $\hat{\sigma} \rightarrow -\hat{\sigma}$) that $T_{pq} = T_{qp}$, and thus the second equality in (2.1).

The psuedo-Liouville operator (2.1) enters the definition of the correlation function $C(k, \vec{v}, \vec{v}_1, t)$ through $\delta f(\vec{k}, \vec{v}, \Gamma(t))$ (see (1.44)). In (1.45) or (1.47) $C(k, \vec{v}, \vec{v}_1, t)$ is obtained as the solution of an equation that, in the spirit of kinetic theory, approximates the exact full N-body dynamics with 2-body dynamics (binary collision approximation). As anticipated in section 1.3, our hard sphere kinetic operator will be obtained for a set of correlation functions, to be defined shortly, rather than for $C(k, \vec{v}, \vec{v}_1, t)$. The reason to make this different choice is the following: the two approaches are equivalent, as will appear below, but our formulation offers a straightforward way to derive the kinetic operator which will be given below; also, it is immediately clear how to make successive better and better approximations in the application of this

operator. Besides, one can easily point out the direction taken in improving the hydrodynamics description. In the following of this section these assertions will be clarified.

2.1.1 The set of correlation functions

Let me introduce a real Hilbert space whose elements are functions of \vec{v}_1 : $f(\vec{v}_1)$. The scalar product between two functions $f(\vec{v}_1)$ and $g(\vec{v}_1)$, denoted by $\langle f(\vec{v}_1), g(\vec{v}_1) \rangle_1$, is defined by:

$$\langle f(\vec{v}_1), g(\vec{v}_1) \rangle_1 = \int d\vec{v}_1 \phi_0(\vec{v}_1) f(\vec{v}_1) g(\vec{v}_1) \quad (2.4)$$

where $\phi_0(\vec{v})$ is the Maxwell velocity distribution function for particles of mass m at temperature $T=1/k_B\beta$:

$$\phi_0(\vec{v}) = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{\beta m}{2} v^2} \quad (2.5)$$

differing from (1.35) by the absence of the factor n , the fluid density, so that $\int d\vec{v} \phi_0(\vec{v}) = 1$. On the left-hand side of (2.4) we can also drop the comma between f and g , interpreting the scalar product as the expectation value of the product fg , with weight ϕ_0 . In this sense also the expression $\langle f(\vec{v}_1) \rangle_1$ acquires a meaning, as the expectation value of f . Before proceeding further, let me make the following remarks, useful for the manipulations in the next subsection. There is a close connection between (2.4) and the canonical average $\langle \dots \rangle = (1/Z) \int d\Gamma e^{-\beta H(\Gamma)} (\dots)$. In fact, the canonical average can more explicitly be written (for smooth potentials) as $\langle \dots \rangle = (1/Q) \int \left[\prod_{p=1}^N d\vec{v}_p \phi_0(\vec{v}_p) \right] \int \left[\prod_{q=1}^N d\vec{r}_q \right] e^{-\beta \Psi} (\dots)$, with $Q = \int \left[\prod_{p=1}^N d\vec{r}_p \right] e^{-\beta \Psi}$, where Ψ is the potential energy of the fluid; for hard spheres the configurational

integral is replaced by $(1/Q) \int \left(\prod_{p=1}^N d\vec{r}_p \right) W(\dots)$ (see note [5] of Chapter 1). Then for example, the canonical average of a function depending only on \vec{v}_1 is $\langle f(\vec{v}_1) \rangle_N = \langle f(\vec{v}_1) \rangle_1$.

I introduce a complete orthonormal set of functions $\psi_\ell(\vec{v})$ ($\ell=1,2,\dots$), whose explicit expressions will be given below; therefore:

$$\langle \psi_\ell(\vec{v}_1), \psi_m(\vec{v}_1) \rangle_1 = \int d\vec{v}_1 \phi_0(\vec{v}_1) \psi_\ell(\vec{v}_1) \psi_m(\vec{v}_1) = \delta_{\ell m} \quad (2.6)$$

Using this complete set I can expand (1.44) in terms of the $\psi_\ell(\vec{v})$:

$$C(k, \vec{v}, \vec{v}_1, t) = N \sum_{\ell} \sum_m F_{\ell m}(k, t) \phi_0(\vec{v}) \phi_0(\vec{v}_1) \psi_\ell(\vec{v}_1) \psi_m(\vec{v}) \quad (2.7)$$

where the coefficients $F_{\ell m}(k, t)$ are given by:

$$F_{\ell m}(k, t) = \frac{1}{N} \int d\vec{v} d\vec{v}_1 \psi_\ell(\vec{v}_1) \psi_m(\vec{v}) C(k, \vec{v}, \vec{v}_1, t) \quad (2.8)$$

(the factors N and $1/N$ in (2.7) and (2.8), respectively, are introduced for convenience). Therefore the knowledge of all the coefficients $F_{\ell m}(k, t)$ is equivalent to the knowledge of $C(k, \vec{v}, \vec{v}_1, t)$. From (1.44), (1.45) and (2.8), one has that the $F_{\ell m}$'s are the following correlation functions:

$$F_{\ell m}(k, t) = \langle a_\ell^*(\vec{k}, \Gamma(0)) a_m(\vec{k}, \Gamma(t)) \rangle_N \quad (2.9)$$

where the dynamical variables $a_\ell(\vec{k}, \Gamma)$ are given by:

$$a_\ell(\vec{k}, \Gamma) = \frac{1}{\sqrt{N}} \sum_{p=1}^N \psi_\ell(\vec{v}_p) e^{-i\vec{k} \cdot \vec{r}_p} \quad (2.10)$$

Therefore I have justified the statement that if we find a kinetic equation for the correlation functions (2.9) we solve a problem equivalent to that of constructing an equation of the type (1.48) for $C(k, \vec{v}, \vec{v}_1, t)$. Anticipating that $\psi_1(\vec{v})=1$, $F(k, t)$, the intermediate scattering function (1.6), is given by $F_{11}(k, t)$. The expression (2.9) can be rewritten as:

$$F_{\ell m}(k, t) = \langle a_\ell^*(\vec{k}, \Gamma) e^{tL} a_m(\vec{k}, \Gamma) \rangle_N \quad (2.11)$$

with L the pseudo-Liouville operator (2.1). All these correlation functions depend only on k , therefore for computational convenience I choose the

vector \vec{k} parallel to the z-axis. Then a complete orthonormal set of functions $\psi_{\ell}(\vec{v})$ is:

$$\psi_{\ell}(\vec{v}) = \psi_{r,s,m}(\vec{v}) = N_{r,s} c^s Y_s^{(m)}(\hat{c}) S_r^{(s+1/2)}(c^2) \quad (2.12)$$

where ℓ stands for the three indices r,s,m ; $\vec{c}=(\beta m/2)^{1/2} \vec{v}$, $c=|\vec{c}|$ and $\hat{c}=\vec{c}/c$; $Y_s^{(m)}$ is the spherical harmonics of order s and index m , and $S_r^{(s+1/2)}$ is the Sonine polynomial of degree r and index $s+1/2$; $N_{r,s}$ is the normalization constant:

$$N_{r,s} = \pi^{3/4} [2\Gamma(r+1)/\Gamma(r+s+3/2)]^{1/2} \quad (2.13)$$

with $\Gamma(x)$ the gamma function. For reference I give the standard definitions.

For the spherical harmonic, if $\hat{c}=(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$:

$$Y_s^{(m)}(\hat{c}) = \frac{(-1)^m}{2^s s!} \left[\frac{(2s+1)(s-m)!}{4\pi(s+m)!} \right]^{1/2} e^{im\phi} \left[(1-x^2)^{m/2} \left(\frac{\partial}{\partial x} \right)^{s+m} (x^2-1)^s \right]_{x=\cos\theta} \quad (2.14)$$

and for the Sonine polynomial:

$$S_r^{(\alpha)}(x) = \frac{1}{r!} x^{-\alpha} e^x \left(\frac{\partial}{\partial x} \right)^r e^{-x} x^{r+\alpha} \quad (2.15)$$

I note that the Sonine polynomials are closely related, through a proportionality factor, to the associated Laguerre polynomials.

For $\ell=1(0,0,0)$, as mentioned above, we have $\psi_1(\vec{v})=1$. As can be easily seen from (2.1), (2.14) and (2.15), all these functions are polynomials in c, c_x, c_y, c_z .

Next I show that we need to consider only the dynamical variables with $m=0$. By symmetry arguments one can show the following: we take two of the dynamical variables a_{ℓ} defined in (2.10), say a_{ℓ_1} and a_{ℓ_2} , with $\ell_1=(r_1, s_1, m_1)$ and $\ell_2=(r_2, s_2, m_2)$; if $m_1 \neq m_2$, the corresponding correlation function $F_{\ell_1 \ell_2}(k, t)$ (see (2.11)) is identically zero, i. e., the two dynamical variables a_{ℓ_1} and a_{ℓ_2} are uncorrelated at all times. I am

ultimately interested in the density-density correlation function $F_{11}(k,t)$, which has $m=0$. Therefore I need to consider only the dynamical variables with $m=0$. Thus, from now on, the index ℓ in $\psi_\ell(\vec{v})$ will stand for the two indices (r,s) , and we will use only the set of functions:

$$\psi_\ell(\vec{v}) = \psi_{r,s,0}(\vec{v}) = N_{r,s} c^{s_Y(0)} \hat{c}^{(s+1/2)}_r c^2 \quad (2.16)$$

This orthonormal set is complete for functions of \vec{v} that depend only on $v=|\vec{v}|$ and v_z , i. e., functions that possess cylindrical symmetry around the z -axis. Now we can see in which sense the hydrodynamic description has been improved. The first three polynomials [1], which are given respectively by $(r,s)=(0,0)$, $(r,s)=(0,1)$ and $(r,s)=(1,0)$, are:

$$\psi_1(\vec{v}) = 1; \quad \psi_2(\vec{v}) = \sqrt{\beta m} v_z; \quad \psi_3(\vec{v}) = \frac{1}{\sqrt{6}} (3 - \beta m v^2) \quad (2.17)$$

From (2.10) we see that the corresponding dynamical variables $a_\ell(\vec{k}, \Gamma)$ are proportional to the space Fourier transform of, respectively, the local density, the local velocity and the local energy (more precisely $\psi_3(\vec{v})$ is the combination of the density and the energy which is orthogonal to both $\psi_1(\vec{v})$ and $\psi_2(\vec{v})$). These correspond to the dynamical variables considered in hydrodynamics, and for which the hydrodynamic equations give the evolution neglecting their coupling with other variables. In our kinetic approximation, instead, the set of three functions $\psi_1(\vec{v}), \psi_2(\vec{v})$ and $\psi_3(\vec{v})$ is extended to a complete orthonormal set of functions $\psi_\ell(\vec{v})$, and the coupling of all the corresponding dynamical variables a_ℓ in (2.10) is considered (although, as remarked, we need only the functions (2.16)).

2.1.2 The kinetic operator

The basic ingredient of our kinetic approximation is to find a function $\phi_\ell(\vec{v})$ corresponding to each $a_\ell(\vec{k}, \Gamma)$ (or, which is the same, to each $\psi_\ell(\vec{v})$) and an operator $L_E(\vec{k})$ acting in the Hilbert space of functions of \vec{v}_1 with the scalar product (2.4), such that each one of the correlation functions (2.11) is approximated by:

$$F_{\ell m}^E(k, t) = \langle \phi_\ell(\vec{v}_1), e^{tL_E(\vec{k})} \phi_m(\vec{v}_1) \rangle_1 \quad (2.18)$$

We require that the kinetic operator $L_E(\vec{k})$ be symmetric, since it can be shown that $F_{\ell m}(k, t)$ is symmetric in the indices ℓ, m (both for smooth potentials and for hard spheres). As stated in section 1.3, we want that both the value and the first time derivative, at time zero, of (2.11) are reproduced exactly by the approximation (2.18). From the orthonormality of the ψ_ℓ 's, and the fact that the first of them is $\psi_1=1$, we easily see from (2.10), (2.11), (1.6) and (1.8) that:

$$F_{\ell m}(k, 0) = \delta_{\ell m} [1 + \delta_{\ell 1} (S(k) - 1)] \quad (2.19)$$

Therefore, if we take:

$$\phi_1(\vec{v}) = \phi_1(\vec{v}; k) = \sqrt{S(k)}; \quad \phi_\ell(\vec{v}) = \psi_\ell(\vec{v}) \quad \ell \geq 2 \quad (2.20)$$

where $\phi_1(\vec{v})$ is a constant function that depends parametrically on k , then (2.19) will be satisfied if $F_{\ell m}$ is replaced by $F_{\ell m}^E$. The second requirement, that the time derivative of the correlation functions, at time zero, is reproduced exactly, is expressed by the equation:

$$\langle a_\ell^*(\vec{k}, \Gamma) L a_m(\vec{k}, \Gamma) \rangle_N = \langle \phi_\ell(\vec{v}_1), L_E(\vec{k}) \phi_m(\vec{v}_1) \rangle_1 \quad (2.21)$$

In the rest of this section the kinetic operator $L_E(\vec{k})$ will be derived from the equality (2.21). I will have to treat separately the case where $\ell, m \geq 2$

and the case where ℓ and/or m is equal to 1. This is due to the particular role played by $\phi_1(\vec{v};k)$: it is the only $\phi_\ell(\vec{v})$ for which $\langle \phi_\ell(\vec{v}_1) \rangle_1 \neq 0$. I will treat first the case $\ell, m \geq 2$.

To shorten the following expressions, let me rewrite (2.2) as:

$$T_{pq} = \int d\hat{\sigma} \delta(\vec{r}_{pq} + \vec{\sigma}) \Theta_{pq}(\hat{\sigma}) \quad (2.22)$$

where:

$$\Theta_{pq}(\hat{\sigma}) = \sigma^2 \theta(\vec{v}_{pq} \cdot \hat{\sigma}) |\vec{v}_{pq} \cdot \hat{\sigma}| [b_{pq}(\hat{\sigma}) - 1] \quad (2.23)$$

Next I compute the left-hand side of (2.21) for $\ell, m \geq 2$. Then:

$$\begin{aligned} \langle a_\ell^*(\vec{k}, \Gamma) L a_m(\vec{k}, \Gamma) \rangle_N &= \frac{1}{N} \left\{ \langle \sum_{p=1}^N \sum_{q=1}^N \psi_\ell(\vec{v}_p) e^{i\vec{k} \cdot \vec{r}_p} \left(\sum_{s=1}^N \vec{v}_s \cdot \frac{\partial}{\partial \vec{r}_s} \right) \psi_m(\vec{v}_q) e^{-i\vec{k} \cdot \vec{r}_q} \rangle_N + \right. \\ &+ \left. \langle \sum_{p=1}^N \sum_{q=1}^N \psi_\ell(\vec{v}_p) e^{i\vec{k} \cdot \vec{r}_p} \left(\frac{1}{2} \sum_{s=1}^N \sum_{t=1}^N T_{st} \right) \psi_m(\vec{v}_q) e^{-i\vec{k} \cdot \vec{r}_q} \rangle_N \right\} \quad (2.24) \end{aligned}$$

In the first term on the right-hand side s must be equal to q , and then, for the orthonormality of the ψ_ℓ 's, p must be equal to q . So this term is equal to (recalling that \vec{k} is parallel to the z -axis):

$$\frac{1}{N} \langle \sum_{p=1}^N \psi_\ell(\vec{v}_p) (-ikv_{pz}) \psi_m(\vec{v}_p) \rangle_N = \langle \psi_\ell(\vec{v}_1) (-ikv_{1z}) \psi_m(\vec{v}_1) \rangle_1 \quad (2.25)$$

In the second term, since T_{st} acts only on the velocities \vec{v}_s and \vec{v}_t , either s or t must be equal to q ; since also $T_{st} = T_{ts}$, I write this term as:

$$\frac{1}{N} \langle \sum_{p=1}^N \sum_{q=1}^N e^{i\vec{k} \cdot (\vec{r}_p - \vec{r}_q)} \psi_\ell(\vec{v}_p) \left(\sum_{s=1}^N T_{sq} \right) \psi_m(\vec{v}_q) \rangle_N \quad (2.26)$$

which, again because of the orthonormality of the ψ_ℓ , is equal to:

$$\frac{1}{N} \left\{ \langle \sum_{p=1}^N \psi_\ell(\vec{v}_p) \left(\sum_{s=1}^N T_{sp} \right) \psi_m(\vec{v}_q) \rangle_N + \langle \sum_{p=1}^N \sum_{q=1}^N e^{i\vec{k} \cdot (\vec{r}_p - \vec{r}_q)} \psi_\ell(\vec{v}_p) T_{pq} \psi_m(\vec{v}_q) \rangle_N \right\} \quad (2.27)$$

The first term of (2.27) is:

$$\begin{aligned} \frac{1}{N} N(N-1) \langle \psi_\ell(\vec{v}_1) T_{21} \psi_m(\vec{v}_1) \rangle_N &= (N-1) \langle \psi_\ell(\vec{v}_1) T_{12} \psi_m(\vec{v}_1) \rangle_N = \\ &= (N-1) \int d\hat{\sigma} \langle \delta(\vec{r}_{12} + \vec{\sigma}) \rangle_N \langle \psi_\ell(\vec{v}_1) \Theta_{12}(\hat{\sigma}) \psi_m(\vec{v}_1) \rangle_N \end{aligned} \quad (2.28)$$

Now, from (1.9) we have that:

$$\langle \delta(\vec{r}_{12} + \vec{\sigma}) \rangle_N = \int d\vec{r}' \langle \delta(\vec{r}_2 - \vec{r}') \delta(\vec{r}_1 - \vec{r}' + \vec{\sigma}) \rangle_N = \int d\vec{r}' \frac{1}{V^2} g(\sigma) = \frac{1}{V} \chi \quad (2.29)$$

with χ the radial distribution function at contact. Therefore, (2.28) is equal to:

$$n\chi \int d\hat{\sigma} \langle \psi_\ell(\vec{v}_1) \Theta_{12}(\hat{\sigma}) \psi_m(\vec{v}_1) \rangle_N \quad (2.30)$$

which, with (2.23), can be written as:

$$\langle \psi_\ell(\vec{v}_1), \Lambda^{(1)} \psi_m(\vec{v}_1) \rangle_1 \quad (2.31)$$

with:

$$\Lambda^{(1)} f(\vec{v}_1) = n\chi \sigma^2 \int d\hat{\sigma} d\vec{v}_2 \phi_0(\vec{v}_2) \theta(\vec{v}_{12} \cdot \hat{\sigma}) |\vec{v}_{12} \cdot \hat{\sigma}| [b_{12}(\hat{\sigma}) - 1] f(\vec{v}_1) \quad (2.32)$$

The second term of (2.27) is:

$$\begin{aligned} \frac{1}{N} N(N-1) \langle e^{i\vec{k} \cdot \vec{r}_{12}} \psi_\ell(\vec{v}_1) T_{12} \psi_m(\vec{v}_2) \rangle_N &= \\ = (N-1) \int d\hat{\sigma} \langle \delta(\vec{r}_{12} + \vec{\sigma}) \rangle_N e^{-i\vec{k} \cdot \vec{\sigma}} \langle \psi_\ell(\vec{v}_1) \Theta_{12}(\hat{\sigma}) \psi_m(\vec{v}_2) \rangle_N \end{aligned} \quad (2.33)$$

which is equal to:

$$\langle \psi_\ell(\vec{v}_1), \Lambda_{\vec{k}}^{(2)} \psi_m(\vec{v}_1) \rangle_1 \quad (2.34)$$

with:

$$\Lambda_{\vec{k}}^{(2)} f(\vec{v}_1) = n\chi \sigma^2 \int d\hat{\sigma} d\vec{v}_2 e^{-i\vec{k} \cdot \vec{\sigma}} \phi_0(\vec{v}_2) \theta(\vec{v}_{12} \cdot \hat{\sigma}) |\vec{v}_{12} \cdot \hat{\sigma}| [b_{12}(\hat{\sigma}) - 1] f(\vec{v}_2) \quad (2.35)$$

Therefore, defining $\Lambda_{\vec{k}} = \Lambda_{\vec{k}}^{(1)} + \Lambda_{\vec{k}}^{(2)}$, (2.20) will be satisfied, for $\ell, m \geq 2$, with:

$$L_E(\vec{k}) = -ikv_{1z} + \Lambda_{\vec{k}}; \quad \ell, m \geq 2 \quad (2.36)$$

To define completely $L_E(\vec{k})$ I have to consider also its matrix elements containing $\psi_1(\vec{v}_1)$. To this purpose I define the projection operator that projects onto $\psi_1(\vec{v}_1)$; using bra-ket notation:

$$P = |\psi_1(\vec{v}_1)\rangle_1 \langle \psi_1(\vec{v}_1)| \quad (2.37)$$

i. e.:

$$Pf(\vec{v}_1) = \int d\vec{v}_1 \phi_0(\vec{v}_1) f(\vec{v}_1) \quad (2.38)$$

With $Q=1-P$, I can write:

$$L_E(\vec{k}) = PL_E(\vec{k})P + PL_E(\vec{k})Q + QL_E(\vec{k})P + QL_E(\vec{k})Q \quad (2.39)$$

The last term, as I have established, is equal to:

$$Q(-ikv_{1z} + \frac{\Lambda}{\vec{k}})Q \quad (2.40)$$

From (2.20), (2.21), and the facts that $T_{pq} a_1(\vec{k}, \Gamma)=0$ and that $\langle v_{1z} \rangle_N=0$, we have that $PL_E(\vec{k})P=0$. To compute $PL_E(\vec{k})Q$ and $QL_E(\vec{k})P$ I use the equality (2.21) with $\ell \geq 2$ and $m=1$. We have then, for the left-hand side of (2.21):

$$\begin{aligned} \langle a_\ell^*(\vec{k}, \Gamma) La_1(\vec{k}, \Gamma) \rangle_N &= \frac{1}{N} \langle \sum_{p=1}^N \sum_{q=1}^N e^{i\vec{k} \cdot (\vec{r}_p - \vec{r}_q)} \psi_\ell(\vec{v}_p) (-ikv_{qz}) \rangle_N = \\ &= \frac{1}{N} \langle \sum_{p=1}^N \psi_\ell(\vec{v}_p) (-ikv_{pz}) \rangle_N = \langle \psi_\ell(\vec{v}_1) (-ikv_{1z}) \rangle_N \end{aligned} \quad (2.41)$$

and for the right-hand side:

$$\langle \phi_\ell(\vec{v}_1), L_E(\vec{k}) \phi_1(\vec{v}_1) \rangle_1 = \sqrt{S(k)} \langle \psi_\ell(\vec{v}_1), QL_E(\vec{k}) P \psi_1(\vec{v}_1) \rangle_1 \quad (2.42)$$

The last term of (2.41) is equal to $\delta_{\ell 2}(-ik/\sqrt{\beta m})$, so that:

$$QL_E(\vec{k})P = - \frac{ik}{\sqrt{\beta m}} \frac{1}{\sqrt{S(k)}} |\psi_2(\vec{v}_1)\rangle_1 \langle \psi_1(\vec{v}_1)| \quad (2.43)$$

Since, as remarked below (2.18), $F_{\ell m}(k, t)=F_{m\ell}(k, t)$, we also have, from (2.41), that:

$$\langle a_1^*(\vec{k}, \Gamma) La_\ell(\vec{k}, \Gamma) \rangle_N = \langle \psi_\ell(\vec{v}_1) (-ikv_{1z}) \rangle_N = - \frac{ik}{\sqrt{\beta m}} \delta_{\ell 2} \quad (2.44)$$

which, by using (2.21) is equal to:

$$\sqrt{S(k)} \langle \psi_1(\vec{v}_1), PL_E(\vec{k}) Q \psi_\ell(\vec{v}_1) \rangle_1 \quad (2.45)$$

Therefore:

$$PL_E(\vec{k})Q = - \frac{ik}{\sqrt{\beta m}} \frac{1}{\sqrt{S(k)}} |\psi_1(\vec{v}_1)\rangle_1 \langle \psi_2(\vec{v}_1)| \quad (2.46)$$

The last step is to compute more explicitly (2.40); with the definition (2.37), we have:

$$\begin{aligned} Q(-ikv_{1z} + \Lambda_{\vec{k}})Q = \\ = (1 - |\psi_1(\vec{v}_1)\rangle_1 \langle\psi_1(\vec{v}_1)|)(-ikv_{1z} + \Lambda_{\vec{k}})(1 - |\psi_1(\vec{v}_1)\rangle_1 \langle\psi_1(\vec{v}_1)|) \end{aligned} \quad (2.47)$$

Since $\langle v_{1z} \rangle_1 = 0$ and $\Lambda_{\vec{k}} \psi_1(\vec{v}_1) = 0$, this expression becomes, remembering that

$\psi_1(\vec{v}_1) = 1$ and $\psi_2(\vec{v}_1) = \sqrt{\beta m} v_z$ (see (2.17)):

$$\begin{aligned} -ikv_{1z} + \frac{ik}{\sqrt{\beta m}} \left[|\psi_2(\vec{v}_1)\rangle_1 \langle\psi_1(\vec{v}_1)| + |\psi_1(\vec{v}_1)\rangle_1 \langle\psi_2(\vec{v}_1)| \right] + \\ + \Lambda_{\vec{k}} - |\psi_1(\vec{v}_1)\rangle_1 \langle\psi_1(\vec{v}_1)| \Lambda_{\vec{k}} \end{aligned} \quad (2.48)$$

The last term can also be written as $\bar{\Lambda}_{\vec{k}}$, where:

$$\bar{\Lambda}_{\vec{k}} f(\vec{v}_1) = \Lambda_{\vec{k}} f(\vec{v}_1) - \langle \Lambda_{\vec{k}} f(\vec{v}_1) \rangle_1 \quad (2.49)$$

Finally, combining (2.39), (2.40), (2.43), (2.46), (2.48), (2.49) and that $PL_E(\vec{k})P=0$, we arrive at:

$$\begin{aligned} L_E(\vec{k}) = -ikv_{1z} + \bar{\Lambda}_{\vec{k}} + \\ + \left(1 - \frac{1}{S(k)} \right) \frac{ik}{\sqrt{\beta m}} \left[|\psi_1(\vec{v}_1)\rangle_1 \langle\psi_2(\vec{v}_1)| + |\psi_2(\vec{v}_1)\rangle_1 \langle\psi_1(\vec{v}_1)| \right] = \\ = -ikv_{1z} + \bar{\Lambda}_{\vec{k}} + A_{\vec{k}} \end{aligned} \quad (2.50)$$

The first term corresponds to the free streaming of the particles; the second term is the collision operator. The last term may be seen as a correction to the free streaming operator, involving the static structure factor $S(k)$; it can be called a mean field operator, because it corrects the free streaming of a particle by a term that depends on the average behavior of the other particles, as contained in $S(k)$. The operator (2.50) is used in (2.18) in our kinetic approximation to the correlation functions.

A remark should be added. Our kinetic approximation is such that the approximated and the exact correlation functions ((2.18) and (2.11) respectively) have the same initial value and the same first time derivative at time zero. But for the particular density-density correlation function $F_{11}(k,t)=F(k,t)$, it is easy to show that $F_{11}^E(k,t)$ gives exactly also the second and third time derivatives at time zero. In fact from (2.1), (2.10), (2.11) and (2.12), it follows that:

$$\frac{d^2 F_{11}(k,t)}{dt^2} = - \frac{k^2}{\beta m} F_{22}(k,t) \quad (2.51)$$

The same equality holds if we replace $F_{11}(k,t)$ and $F_{22}(k,t)$ with their corresponding approximations given by (2.18), as follows from the explicit expression of $L_E(\vec{k})$. Therefore, since the initial value and the first time derivative at time zero of $F_{22}(k,t)$ are reproduced exactly, so will be the second and the third time derivatives, at time zero, of $F_{11}(k,t)$. This means that the function we are interested in, the intermediate scattering function $F(k,t)$, is approximated better than the other correlation functions.

2.2 The BGK method

For computational convenience it is better to use the orthonormal set ψ_ℓ rather than ϕ_ℓ . So, instead of (2.18) I consider the functions:

$$\bar{F}_{\ell m}^E(k,t) = \langle \psi_\ell(\vec{v}_1), e^{tL_E(\vec{k})} \psi_m(\vec{v}_1) \rangle_1 \quad (2.52)$$

Then, we have $F(k,t)=F_{11}^E(k,t)=S(k)\bar{F}_{11}^E(k,t)$. In the calculations I compute the Laplace transforms of (2.52), i. e.:

$$\tilde{S}_{\ell m}^E(k,z) = \int_0^\infty dt e^{-zt} \bar{F}_{11}^E(k,t) = \langle \psi_\ell(\vec{v}_1), \frac{1}{z-L_E(\vec{k})} \psi_\ell(\vec{v}_1) \rangle_1 \quad (2.53)$$

Therefore to compute the $\bar{F}_{11}^E(k, t)$ one has to be able to invert the operator $z - L_E(\vec{k})$. In order to do that, the Bhatnagar-Gross-Krook (BGK) approximation is used for $L_E(\vec{k})$. Then, in the BGK approximation of order M, the free streaming and the mean field operators are taken into account exactly, while the collision operator is approximated by:

$$\bar{L}_{\vec{k}} = \sum_{\ell=1}^M \sum_{m=1}^M |\psi_{\ell}(\vec{v}_1)\rangle_1 \Omega_{\ell m}(k) {}_1\langle\psi_m(\vec{v}_1)| + d(k) \sum_{\ell=M+1}^{\infty} |\psi_{\ell}(\vec{v}_1)\rangle_1 {}_1\langle\psi_m(\vec{v}_1)| \quad (2.54)$$

where:

$$\Omega_{\ell m}(k) = \langle\psi_{\ell}(\vec{v}_1), \bar{L}_{\vec{k}} \psi_m(\vec{v}_1)\rangle_1 \quad (2.55)$$

In other words, the first MxM block of the matrix of the collision operator, with respect to the set $\psi_{\ell}(\vec{v})$, is taken into account exactly, while the other matrix elements are set equal to zero, except for the diagonal elements, $\ell=m=M+1, M+2, \dots$, which are all set equal to a constant $d(k)$, chosen to be equal to $\Omega_{M+1, M+1}(k)$. It can be shown that all the diagonal elements $\Omega_{\ell\ell}(k)$ are real and non positive. The precise choice of $d(k)$, as long as M is not very small, is not expected to affect appreciably the results. This is in agreement with what I found, also in the case of binary mixtures [2].

With a little manipulation, the operator $L_E(\vec{k})$ so approximated can now be written in the form:

$$L_E(\vec{k}) = f(\vec{k}) + F(\vec{k}) \quad (2.56)$$

where:

$$f(\vec{k}) = -ikv_{1z} + d(k)$$

is a multiplicative operator, and $F(\vec{k})$ is a finite dimensional MxM matrix operator:

$$F(\vec{k}) = \sum_{\ell=1}^M \sum_{m=1}^M |\psi_{\ell}(\vec{v}_1)\rangle_1 H_{\ell m}(k) {}_1\langle\psi_m(\vec{v}_1)| \quad (2.57)$$

with:

$$H_{\ell m}(k) = \langle\psi_{\ell}(\vec{v}_1), (\bar{\Lambda}_{\vec{k}} + A_{\vec{k}})\psi_m(\vec{v}_1)\rangle_1 - d(k)\delta_{\ell m} \quad (2.58)$$

From the operator identity:

$$\frac{1}{z - (f(\vec{k}) + F(\vec{k}))} = \frac{1}{z - f(\vec{k})} + \frac{1}{z - f(\vec{k})} F(\vec{k}) \frac{1}{z - (f(\vec{k}) + F(\vec{k}))} \quad (2.59)$$

we get, for $\ell, m \leq M$:

$$\tilde{S}_{\ell m}^E(k, z) = \left[\frac{1}{z - L_E(\vec{k})} \right]_{\ell m} = \left[\frac{1}{1 - A(k, z)H(k)} A(k, z) \right]_{\ell m} \quad (2.60)$$

where $H(k)$ is the $M \times M$ matrix with elements (2.58), and $A(k, z)$ is the $M \times M$ matrix with elements:

$$A_{\ell m}(k, z) = \langle\psi_{\ell}(\vec{v}_1), \frac{1}{z + ikv_{1z} - d(k)}\psi_m(\vec{v}_1)\rangle_1 \quad (2.61)$$

The operations implicit in the last term in (2.60) have to be understood as operations between $M \times M$ matrices. The fact that $F(\vec{k})$ is a finite dimensional $M \times M$ matrix operator allows to compute the $\tilde{S}_{\ell m}^E(k, z)$ for $\ell, m \leq M$ using only an $M \times M$ matrix, although this matrix implicitly contains the contribution of the ∞ dimensional operator $f(\vec{k})$.

It is also possible to evaluate the functions $\tilde{S}_{\ell m}^E(k, z)$ in terms of the discrete eigenvalues of $L_E(\vec{k})$. These are associated with the poles of the resolvent operator $[z - L_E(\vec{k})]^{-1}$, namely with the M values $z = z_n(k)$ ($n=1, 2, \dots, M$) for which:

$$D(k, z) = \det [I - A(k, z)H(k)] = 0 \quad (2.62)$$

Then, it is shown in Appendix I that (2.60) is replaced by:

$$\tilde{S}_{\ell m}^E(k, z) = \sum_{n=1}^M \frac{M_{\ell m, n}(k)}{z - z_n(k)} \quad (2.63)$$

where the $z_n(k)$ are the eigenvalues and the $M_{\ell m, n}(k)$ are the corresponding amplitudes, given by:

$$M_{\ell m, n}(k) = \frac{1}{D'(k, z_n(k))} \left[G(k, z_n(k)) A(k, z_n(k)) \right]_{\ell m} \quad (2.64)$$

where G is the transpose of the matrix of cofactors of $I-AH$ and

$$D'(k, z_n(k)) = \left. \frac{dD(k, z)}{dz} \right|_{z=z_n(k)} \quad (2.65)$$

The difference between (2.63) and the exact expression (2.60) is that in (2.63) the essential singularity of $\tilde{S}_{\ell m}^E(k, z)$ for $\text{Re } z = -\infty$ has been neglected. This singularity stems from the matrix elements (2.61), as will be shown in the next chapter, dedicated to the calculation of the matrix elements.

The above shows that there is a natural way to make successive approximations, by increasing the number M , thus treating the collision operator better and better. This proves one of the assertions made at the end of the introduction to this section.

2.3 Extension to binary mixtures

Everything that has been explained so far in this chapter for simple fluids is readily generalized to binary mixtures. The introduction of the kinetic approximation follows the same procedure, and also the method of computation (the BGK method) is the same. However, the notation, for obvious reasons, becomes unavoidably more cumbersome. Here I will reproduce the basic formulas for the case of binary mixtures, corresponding to those of the previous section, but I will not repeat the derivations. The main difference from the case of simple fluids is that the elements of the Hilbert space are now two component functions.

2.3.1 The correlation functions and the kinetic operator

The hard sphere potential between two hard spheres, of diameter σ_1 and σ_2 respectively, is infinite for distances between their centers smaller than or equal to $\sigma_{12}=(\sigma_1+\sigma_2)/2$, which is the distance at contact.

For a hard sphere fluid with N_1 particles of mass m_1 and diameter σ_1 and N_2 particles of mass m_2 and diameter σ_2 , the pseudo-Liouville operator that generalizes (2.1) is:

$$L = \sum_{i=1}^2 \sum_{p=1}^{N_i} \vec{v}_p^{(i)} \cdot \frac{\partial}{\partial \vec{r}_p^{(i)}} + \frac{1}{2} \sum_{i=1}^2 \sum_{j=1}^2 \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} T_{pq}^{(i,j)} \quad (2.66)$$

The collision operator $T_{pq}^{(i,j)}$ describes a binary collision between particle p of species i and particle q of species j . It is given by:

$$T_{pq}^{(i,j)} = \sigma_{ij}^2 \int d\hat{\sigma} \delta(\vec{r}_{pq}^{(i,j)} + \hat{\sigma}) \theta(\vec{v}_{pq}^{(i,j)} \cdot \hat{\sigma}) |\vec{v}_{pq}^{(i,j)} \cdot \hat{\sigma}| [b_{pq}^{(i,j)}(\hat{\sigma}) - 1] \quad (2.67)$$

where $\sigma_{ij}=(\sigma_i+\sigma_j)/2$, $\vec{\sigma}^{(i,j)}=\sigma_{ij}\hat{\sigma}$, $\vec{r}_{pq}^{(i,j)}=\vec{r}_p^{(i)}-\vec{r}_q^{(j)}$, $\vec{v}_{pq}^{(i,j)}=\vec{v}_p^{(i)}-\vec{v}_q^{(j)}$, and the substitution operator $b_{pq}^{(i,j)}(\hat{\sigma})$, which transforms the precollisional velocities into the postcollisional velocities, is given by:

$$\begin{aligned} b_{pq}^{(i,j)}(\hat{\sigma}) \vec{v}_p^{(i)} &= \vec{v}_p^{(i)'} = \vec{v}_p^{(i)} - 2 \frac{\mu_{ij}}{m_i} (\vec{v}_{pq}^{(i,j)} \cdot \hat{\sigma}) \hat{\sigma} \\ b_{pq}^{(i,j)}(\hat{\sigma}) \vec{v}_q^{(j)} &= \vec{v}_q^{(j)'} = \vec{v}_q^{(j)} + 2 \frac{\mu_{ij}}{m_j} (\vec{v}_{pq}^{(i,j)} \cdot \hat{\sigma}) \hat{\sigma} \end{aligned} \quad (2.68)$$

with $\mu_{ij}=m_i m_j / (m_i + m_j)$.

Now, instead of (2.11), our set of correlation functions will be:

$$F_{\ell m}^{(i,j)}(\vec{k}, t) = \langle a_{\ell}^{(i)*}(\vec{k}, \Gamma) e^{tL} a_m^{(j)}(\vec{k}, \Gamma) \rangle_N \quad (2.69)$$

where the dynamical variables $a_{\ell}^{(i)}(\vec{k}, \Gamma)$ are:

$$a_{\ell}^{(i)}(\vec{k}, \Gamma) = \frac{1}{\sqrt{N_i}} \sum_{p=1}^{N_i} \psi_{\ell}^{(i)}(\vec{v}_p^{(i)}) e^{-i\vec{k} \cdot \vec{r}_p^{(i)}} \quad (2.70)$$

The set of functions $\psi_{\ell}^{(i)}(\vec{v})$ is given, for each $i=1,2$, by (2.16), with $\vec{c}=(\beta m_i/2)^{1/2} \vec{v}$. The orthonormality relation is:

$$\int d\vec{v} \phi_0^{(i)}(\vec{v}) \psi_{\ell}^{(i)}(\vec{v}) \psi_m^{(i)}(\vec{v}) = \delta_{\ell m} \quad (2.71)$$

where $\phi_0^{(i)}(\vec{v})$ is the Maxwell distribution for particles of species i :

$$\phi_0^{(i)}(\vec{v}) = \left(\frac{\beta m_i}{2\pi}\right)^{3/2} e^{-\frac{\beta m_i}{2} v^2} \quad (2.72)$$

The partial intermediate scattering functions (1.13) will be given by $F_{ij}(k, t) = F_{11}^{(i,j)}(k, t)$. The initial values of the correlation functions (2.69), using (2.70), (2.71) and (1.15), are given by:

$$F_{\ell m}^{(i,j)}(k, 0) = \delta_{\ell m} [\delta_{ij} + \delta_{\ell 1} (S_{ij}(k) - 1)] \quad (2.73)$$

For later use, in section 2.4, I remark that, with the use of $a_{\ell}^{(1)}(\vec{k}, \Gamma)$ and $a_{\ell}^{(2)}(\vec{k}, \Gamma)$, one can build the dynamical variable:

$$a'_{\ell}(\vec{k}, \Gamma) = \frac{1}{\sqrt{N}} \left[\sum_{p=1}^{N_1} \psi_{\ell}^{(1)}(\vec{v}_p^{(1)}) e^{-i\vec{k} \cdot \vec{r}_p^{(1)}} + \sum_{q=1}^{N_2} \psi_{\ell}^{(2)}(\vec{v}_q^{(2)}) e^{-i\vec{k} \cdot \vec{r}_q^{(2)}} \right] \quad (2.74)$$

analogous, in a certain sense, to $a_{\ell}(\vec{k}, \Gamma)$ for simple fluids.

Since for each ℓ we have two dynamical variables, we are led naturally to the introduction of a Hilbert space whose elements $\vec{\phi}$ are two-component functions, in order to make a kinetic approximation of the correlation functions (2.69):

$$\vec{\phi}(\vec{v}_1, \vec{v}_2) = \begin{pmatrix} \phi_1(\vec{v}_1) \\ \phi_2(\vec{v}_2) \end{pmatrix} \quad (2.75)$$

where the components $\phi_1(\vec{v}_1)$ and $\phi_2(\vec{v}_2)$ depend on \vec{v}_1 and \vec{v}_2 respectively. The scalar product $\langle\langle \dots \rangle\rangle_{1>2}$ is defined by:

$$\begin{aligned} \langle\langle \vec{\phi}(\vec{v}_1, \vec{v}_2), \vec{\phi}'(\vec{v}_1, \vec{v}_2) \rangle\rangle_{1>2} &= \int d\vec{v}_1 \phi_0^{(1)}(\vec{v}_1) \int d\vec{v}_2 \phi_0^{(2)}(\vec{v}_2) \times \\ &\times [\phi_1(\vec{v}_1) \phi_1'(\vec{v}_1) + \phi_2(\vec{v}_2) \phi_2'(\vec{v}_2)] \end{aligned} \quad (2.76)$$

In analogy with simple fluids, with this scalar product, also the expression $\langle\langle\vec{\phi}(\vec{v}_1, \vec{v}_2)\rangle\rangle_1 \rangle_2$ has a meaning, as the expectation value of $\vec{\phi}(\vec{v}_1, \vec{v}_2)$.

A general operator C in this Hilbert space, that transforms a function $\vec{\phi}(\vec{v}_1, \vec{v}_2)$ into $\vec{\phi}'(\vec{v}_1, \vec{v}_2) = C\vec{\phi}(\vec{v}_1, \vec{v}_2)$ has the following matrix notation:

$$\begin{pmatrix} \phi'_1(\vec{v}_1) \\ \phi'_2(\vec{v}_2) \end{pmatrix} = \begin{pmatrix} C^{(1,1)} & C^{(1,2)} \\ C^{(2,1)} & C^{(2,2)} \end{pmatrix} \begin{pmatrix} \phi_1(\vec{v}_1) \\ \phi_2(\vec{v}_2) \end{pmatrix} \quad (2.77)$$

It should be kept in mind that the 2x2 matrix nature only applies to the component indices i, j of $C^{(i,j)}$, but that each $C^{(i,j)}$, and thus also C , if expressed in a matrix representation, requires an $\infty \times \infty$ matrix.

I note that the set of functions:

$$\vec{\psi}_\ell^{(1)}(\vec{v}_1, \vec{v}_2) = \begin{pmatrix} \psi_\ell^{(1)}(\vec{v}_1) \\ 0 \end{pmatrix} \quad \ell=1, 2, \dots \quad (2.78)$$

$$\vec{\psi}_\ell^{(2)}(\vec{v}_1, \vec{v}_2) = \begin{pmatrix} 0 \\ \psi_\ell^{(2)}(\vec{v}_2) \end{pmatrix}$$

constitutes a complete orthonormal set (in the scalar product (2.76)) for functions $\vec{\phi}(\vec{v}_1, \vec{v}_2)$ depending only on $v_1 = |\vec{v}_1|$, v_{1z} , $v_2 = |\vec{v}_2|$ and v_{2z} .

In a completely similar manner as for simple fluids I want to find a function $\vec{\phi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2)$ corresponding to each $a_\ell^{(i)}(\vec{k}, \Gamma)$, and an operator $L_E(\vec{k})$ such that the $F_{\ell m}^{(i,j)}$ of (2.69) are approximated by:

$$F_{\ell m}^{(i,j)E}(k, t) = \langle\langle \vec{\phi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2) e^{tL_E(\vec{k})} \vec{\phi}_m^{(j)}(\vec{v}_1, \vec{v}_2) \rangle\rangle_1 \rangle_2 \quad (2.79)$$

where the initial values and the first time derivatives, at time zero, of (2.69) are reproduced exactly. Here I only give the results. For $\ell \geq 2$ we have that:

$$\vec{\phi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2) = \vec{\psi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2) \quad (i=1, 2) \quad (2.80)$$

with $\psi_\ell^{(i)}(\vec{v}_1, \vec{v}_2)$ given by (2.78); for $\ell=1$ we obtain two (constant) functions depending parametrically on k [3]:

$$\vec{\phi}_1^{(1)}(\vec{v}_1, \vec{v}_2; k) = \left(\begin{matrix} [S_{11}(k)]^{1/2} \cos \alpha(k) \\ [S_{11}(k)]^{1/2} \sin \alpha(k) \end{matrix} \right) \quad (2.81)$$

$$\vec{\phi}_1^{(2)}(\vec{v}_1, \vec{v}_2; k) = \left(\begin{matrix} [S_{22}(k)]^{1/2} \sin \alpha(k) \\ [S_{22}(k)]^{1/2} \cos \alpha(k) \end{matrix} \right)$$

where:

$$\alpha(k) = \frac{1}{2} \arcsin \frac{S_{12}(k)}{\sqrt{S_{11}(k)S_{22}(k)}}. \quad (2.82)$$

In the matrix notation (2.77) the "elements" of the kinetic operator $L_E(\vec{k})$ are given by:

$$L_E^{(i,j)}(\vec{k}) = \delta_{ij}(-ik v_{iz}) + \bar{\Lambda}_{\vec{k}}^{(i,j)} + A_{\vec{k}}^{(i,j)} \quad (2.83)$$

I note that, in transforming any function $\vec{\phi}(\vec{v}_1, \vec{v}_2)$ into $\vec{\phi}'(\vec{v}_1, \vec{v}_2) = L_E(\vec{k})\vec{\phi}(\vec{v}_1, \vec{v}_2)$, $L_E^{(i,j)}(\vec{k})$ acts on the component j of $\vec{\phi}$, which depends on \vec{v}_j , and yields a function of \vec{v}_i that contributes to the i -th component of $\vec{\phi}'$; i. e.:

$$\begin{aligned} \phi'_1(\vec{v}_1) &= L_E^{(1,1)}(\vec{k})\phi_1(\vec{v}_1) + L_E^{(1,2)}(\vec{k})\phi_2(\vec{v}_2) \\ \phi'_2(\vec{v}_2) &= L_E^{(2,1)}(\vec{k})\phi_1(\vec{v}_1) + L_E^{(2,2)}(\vec{k})\phi_2(\vec{v}_2) \end{aligned} \quad (2.84)$$

Expression (2.83) is the analogue, for binary mixtures, of (2.50). The first term represents free streaming. The second term contains the collision operators; we have:

$$\bar{\Lambda}_{\vec{k}}^{(i,j)} f(\vec{v}_j) = \Lambda_{\vec{k}}^{(i,j)} f(\vec{v}_j) - \int d\vec{v}_i \phi_0^{(i)}(\vec{v}_i) \Lambda_{\vec{k}}^{(i,j)} f(\vec{v}_j) \quad (2.85)$$

with:

$$\begin{aligned}\Lambda_{\vec{k}}^{(i,i)} &= {}^{(1)}\Lambda_{\vec{k}}^{(i,i)} + {}^{(2)}\Lambda_{\vec{k}}^{(i,i)} \quad i=1,2 \\ \Lambda_{\vec{k}}^{(i,j)} &= {}^{(2)}\Lambda_{\vec{k}}^{(i,j)} \quad i \neq j\end{aligned}\quad (2.86)$$

where:

$$\begin{aligned}{}^{(1)}\Lambda_{\vec{k}}^{(i,i)} f(\vec{v}_i) &= \sum_{i'=1}^2 n_{i'} \chi_{ii'} \sigma_{ii'}^2 \int d\sigma d\vec{v}_3 \hat{\sigma} \cdot \vec{v}_3^{(i')} \phi_0^{(i')}(\vec{v}_3^{(i')}) |\vec{v}_{i3}^{(i,i')} \cdot \hat{\sigma}| \times \\ &\times \theta(\vec{v}_{i3}^{(i,i')} \cdot \hat{\sigma}) [b_{i3}^{(i,i')}(\hat{\sigma}) - 1] f(\vec{v}_i^{(i)})\end{aligned}\quad (2.87)$$

with $n_i = N_i/V$ the number density of particles of species i and $\chi_{ij} = g_{ij}(\sigma_{ij})$ the radial distribution function at contact;

$$\begin{aligned}{}^{(2)}\Lambda_{\vec{k}}^{(i,j)} f(\vec{v}_j) &= \sqrt{n_i n_j} \chi_{ij} \sigma_{ij}^2 \int d\sigma d\vec{v}_3 e^{-i\vec{k} \cdot \vec{\sigma}} \phi_0^{(j)}(\vec{v}_3^{(j)}) |\vec{v}_{i3}^{(i,j)} \cdot \hat{\sigma}| \times \\ &\times \theta(\vec{v}_{i3}^{(i,j)} \cdot \hat{\sigma}) [b_{i3}^{(i,j)}(\hat{\sigma}) - 1] f(\vec{v}_j^{(j)}).\end{aligned}\quad (2.88)$$

The superscripts (1) and (2) on the left of the Λ 's correspond to parts which are, respectively, independent of \vec{k} and dependent on \vec{k} . The third term in (2.83) represents the mean field operators:

$$\begin{aligned}A_{\vec{k}}^{(i,j)} f(\vec{v}_j) &= \int d\vec{v}_j^{(j)} \phi_0^{(j)}(\vec{v}_j^{(j)}) [m^{(i,j)}(k) \psi_2^{(i)}(\vec{v}_i^{(i)}) \psi_1^{(j)}(\vec{v}_j^{(j)}) + \\ &+ m^{(j,i)}(k) \psi_1^{(i)}(\vec{v}_i^{(i)}) \psi_2^{(j)}(\vec{v}_j^{(j)})] f(\vec{v}_j^{(j)})\end{aligned}\quad (2.89)$$

with:

$$m^{(i,j)} = \delta_{ij} \frac{ik}{\sqrt{\beta m_i}} + B^{(i,j)}(k) \quad (2.90)$$

and:

$$\begin{aligned}B^{(1,1)}(k) &= - \frac{ik}{\sqrt{\beta m_1}} \left[\frac{S_{22}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)} \right]^{1/2} \cos \alpha(k) \\ B^{(1,2)}(k) &= \frac{ik}{\sqrt{\beta m_1}} \left[\frac{S_{22}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)} \right]^{1/2} \sin \alpha(k) \\ B^{(2,1)}(k) &= \frac{ik}{\sqrt{\beta m_2}} \left[\frac{S_{11}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)} \right]^{1/2} \sin \alpha(k) \\ B^{(2,2)}(k) &= - \frac{ik}{\sqrt{\beta m_2}} \left[\frac{S_{11}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)} \right]^{1/2} \cos \alpha(k)\end{aligned}\quad (2.91)$$

In (2.82) and (2.91) I have used the Schwarz inequality (1.17) and that $S_{11}(k)$ and $S_{22}(k)$ are positive.

Like for simple fluids, the approximation $F_{11}^{(i,j)E}(k,t)$ reproduces exactly also the second and the third time derivatives, at time zero, of the $F_{ij}(k,t)=F_{11}^{(i,j)}(k,t)$.

2.3.2 The BGK method

In analogy with simple fluids, let me define:

$$\bar{F}_{lm}^{(i,j)E}(k,t) = \langle \langle \vec{\psi}_l^{(i)}(\vec{v}_1, \vec{v}_2) e^{tL_E(\vec{k})} \vec{\psi}_m^{(j)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2. \quad (2.92)$$

Then, from (2.81), it follows that:

$$\begin{aligned} F_{11}(k,t) &= F_{11}^{(1,1)E}(k,t) = S_{11}(k) \left[\bar{F}_{11}^{(1,1)E}(k,t) \cos^2 \alpha(k) + \bar{F}_{11}^{(2,2)E}(k,t) \sin^2 \alpha(k) + \right. \\ &\quad \left. + 2\bar{F}_{11}^{(1,2)E}(k,t) \sin \alpha(k) \cos \alpha(k) \right] \\ F_{22}(k,t) &= F_{11}^{(2,2)E}(k,t) = S_{22}(k) \left[\bar{F}_{11}^{(1,1)E}(k,t) \sin^2 \alpha(k) + \bar{F}_{11}^{(2,2)E}(k,t) \cos^2 \alpha(k) + \right. \\ &\quad \left. + 2\bar{F}_{11}^{(1,2)E}(k,t) \sin \alpha(k) \cos \alpha(k) \right] \\ F_{12}(k,t) &= F_{11}^{(1,2)E}(k,t) = \left[S_{11}(k) S_{22}(k) \right]^{1/2} \left[\left(\bar{F}_{11}^{(1,1)E}(k,t) + \bar{F}_{11}^{(2,2)E}(k,t) \right) \cos \alpha(k) \times \right. \\ &\quad \left. + \bar{F}_{11}^{(1,2)E}(k,t) \sin \alpha(k) \right] \end{aligned} \quad (2.93)$$

The Laplace transform of (2.92) is:

$$\begin{aligned} \tilde{S}_{lm}^{(i,j)E}(k,z) &= \int_0^\infty dt e^{-zt} \bar{F}_{lm}^{(i,j)E}(k,t) = \\ &= \langle \langle \vec{\psi}_l^{(i)}(\vec{v}_1, \vec{v}_2) \frac{1}{z - L_E(\vec{k})} \vec{\psi}_m^{(j)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 \end{aligned} \quad (2.94)$$

In the BGK approximation of order M, the first $2M \times 2M$ block ($\ell, m=1, 2, \dots, M$; $i, j=1, 2$) of the ∞ matrix representation of the collision operator $\bar{\Lambda}_{\vec{k}}$ ($\bar{\Lambda}_{\vec{k}}$ is the operator whose "elements" are the $\bar{\Lambda}_{\vec{k}}^{(i,j)}$, like in (2.77)) is taken into account exactly, while the other matrix elements are set equal to zero, except for the diagonal elements, $\ell=m=M+1, M+2, \dots$, and $i=j$, which are all set equal to a constant $d(k)$; i. e.:

$$\begin{aligned} \bar{\Lambda}_{\vec{k}} = & \sum_{i=1}^2 \sum_{\ell=1}^M \sum_{j=1}^2 \sum_{m=1}^M |\vec{\psi}_{\ell}^{(i)}(\vec{v}_1, \vec{v}_2) \rangle_1 \langle_2 \Omega_{\ell m}^{(i,j)}(k) \langle_1 \langle_2 \langle \vec{\psi}_m^{(j)}(\vec{v}_1, \vec{v}_2) | + \\ & + d(k) \sum_{\ell=1}^M \sum_{m=1}^M |\vec{\psi}_{\ell}^{(i)}(\vec{v}_1, \vec{v}_2) \rangle_1 \langle_2 \langle_1 \langle_2 \langle \vec{\psi}_m^{(j)}(\vec{v}_1, \vec{v}_2) | \end{aligned} \quad (2.95)$$

with:

$$\Omega_{\ell m}^{(i,j)}(k) = \langle \langle \vec{\psi}_m^{(i)}(\vec{v}_1, \vec{v}_2), \bar{\Lambda}_{\vec{k}} \vec{\psi}_m^{(j)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 \quad (2.96)$$

The constant $d(k)$ is chosen to be:

$$d(k) = x_1 \langle \psi_{M+1}^{(1)}(\vec{v}_1) \bar{\Lambda}_{\vec{k},1} \psi_{M+1}^{(1)}(\vec{v}_1) \rangle_1 + x_2 \langle \psi_{M+1}^{(2)}(\vec{v}_2) \bar{\Lambda}_{\vec{k},1} \psi_{M+1}^{(2)}(\vec{v}_2) \rangle_2 \quad (2.97)$$

where, in this formula, $\bar{\Lambda}_{\vec{k},1}$ denotes the simple fluid collision operator in (2.50). There are other possible choices for $d(k)$; for example, we could have chosen two different $d(k)$, i. e. $d_1(k)$ and $d_2(k)$, respectively for the diagonal matrix elements with $\ell=m>M$ and $i=j=1$, and $\ell=m>M$ and $i=j=2$. However, the results for the dynamic structure factors $S_{ij}(k, \omega)$, the quantities in which I am interested, are not sensitive to this choice, in the sense that its effect is negligible, already for $M \geq 5$.

In analogy with (2.56) we have:

$$L_E(\vec{k}) = f(\vec{k}) + F(\vec{k}) \quad (2.98)$$

The "elements" of the operators $f(\vec{k})$ and $F(\vec{k})$ are given by:

$$f^{(i,j)}(\vec{k}) = \delta_{ij} [-ik v_{iz} + d(k)] \quad (2.99)$$

and:

$$F(\vec{k}) = \sum_{i=1}^2 \sum_{\ell=1}^M \sum_{j=1}^2 \sum_{m=1}^M |\vec{\psi}_{\ell}^{(i)}(\vec{v}_1, \vec{v}_2)_{>1>2} H_{\ell m}^{(i,j)}(k) {}_{1<2}< \vec{\psi}_m^{(j)}(\vec{v}_1, \vec{v}_2)| \quad (2.100)$$

with:

$$H_{\ell m}^{(i,j)}(k) = \langle \langle \vec{\psi}_m^{(j)}(\vec{v}_1, \vec{v}_2), (\vec{\Lambda}_{\vec{k}} + A_{\vec{k}}) \vec{\psi}_{\ell}^{(i)}(\vec{v}_1, \vec{v}_2)_{>1>2} - d(k) \delta_{\ell m} \delta_{ij} \rangle \rangle \quad (2.101)$$

In the bra-ket notation employed in (2.95) and (2.100) $|\vec{\psi}_{\ell}^{(i)}(\vec{v}_1, \vec{v}_2)_{>1>2}$ is a column vector with the two elements $\psi_{\ell}^{(1)}(\vec{v}_1)$ and $\psi_{\ell}^{(2)}(\vec{v}_2)$, and ${}_{1<2}< \vec{\psi}_m^{(j)}(\vec{v}_1, \vec{v}_2)|$ is a row vector, with the same two elements. In analogy with (2.60) and (2.61), we have:

$$\tilde{S}_{\ell m}^{(i,j)E}(k, z) = \left[\frac{1}{1 - A(k, z)H(k)} A(k, z) \right]_{\ell m}^{(i,j)} \quad (2.102)$$

where:

$$A_{\ell m}^{(i,j)}(k, z) = \delta_{ij} \langle \langle \vec{\psi}_{\ell}^{(i)}(\vec{v}_1, \vec{v}_2) \frac{1}{z + ikv_{iz} - d(k)} \vec{\psi}_m^{(i)}(\vec{v}_1, \vec{v}_2)_{>1>2} \rangle \rangle \quad (2.103)$$

and $A(k, z)$ and $H(k)$ in (2.102) are $2M \times 2M$ matrices.

The discrete eigenvalues of $L_E(\vec{k})$ are given by the $2M$ values $z = z_n(k)$ ($n=1, 2, \dots, 2M$) for which:

$$D(k, z) = \det[I - A(k, z)H(k)] = 0 \quad (2.104)$$

so that (2.102) is replaced by:

$$\tilde{S}_{\ell m}^{(i,j)E}(k, z) = \sum_{n=1}^{2M} \frac{M_{\ell m, n}^{(i,j)}(k)}{z - z_n(k)} \quad (2.105)$$

with:

$$M_{\ell m, n}^{(i,j)} = \frac{1}{D' [k, z_n(k)]} [G(k, z_n(k)) A(k, z_n(k))]_{\ell m}^{(i,j)} \quad (2.106)$$

where G is the transpose of the matrix of cofactors of $I - AH$ and:

$$D' [k, z_n(k)] = \left. \frac{dD(k, z)}{dz} \right|_{z=z_n(k)} \quad (2.107)$$

Like for simple fluids, in going from (2.102) to (2.105) the essential singularity for $\text{Re } z = -\infty$ has been neglected.

In the approximation (2.105), the correlation functions $\bar{F}_{\ell m}^{(i,j)E}(k,t)$, which are the inverse Laplace transform of $\tilde{S}_{\ell m}^{(i,j)E}(k,z)$:

$$\bar{F}_{\ell m}^{(i,j)E}(k,t) = \frac{1}{2\pi i} \int_{-i\infty+z_0}^{i\infty+z_0} dz \tilde{S}_{\ell m}^{(i,j)E}(k,z) \quad (2.106a)$$

where z_0 is a real number larger than the real part of any singularity of $\tilde{S}_{\ell m}^{(i,j)E}(k,z)$, are given by:

$$\bar{F}_{\ell m}^{(i,j)E}(k,t) = \sum_{n=1}^{2M} M_{\ell m,n}^{(i,j)}(k) e^{z_n(k)t} \quad (2.106b)$$

The eigenvalues obtained from (2.104) and the corresponding amplitudes (2.106) will be important quantities in the exposition of the results.

2.4 Simple fluid limit

In this section I want to verify that the above formulas properly reduce to those of a simple component fluid. This section is not needed for the rest of the thesis. It has been included because it presents the interesting result, in the second subsection, that together with a proper reduction to the simple component, we get also the self correlation functions, to be introduced below, that, in the usual kinetic theory of simple fluids, require the use of a kinetic operator different from (2.50).

I will show how the simple fluid correlation functions are recovered when, in the binary mixture, we take the limit of single component. There are formally two ways in which this can be achieved: either one of the two partial densities, n_1 or n_2 , goes to zero, or the two components become identical, i. e. $\sigma_1=\sigma_2=\sigma$ and $m_1=m_2=m$. In this section I use the notation L_1 to denote the simple fluid pseudo-Liouville operator (2.1), while I keep the

notation L for the corresponding binary mixture operator (2.66). Accordingly, I use $\bar{\Lambda}_{\vec{k},1}$, $A_{\vec{k},1}$ and $L_{E,1}(\vec{k})$ for, respectively, the simple fluid collision, mean field, and full kinetic operators in (2.50). For binary mixtures I retain the notations of the previous section.

2.4.1 Limit $n_2 \rightarrow 0$

Here I will show that it is straightforward to verify that, when $n_2 \rightarrow 0$, we recover immediately the correlation functions $F_{\ell m}(k, t)$ for simple fluids. First I will derive the limit for the kinetic operator $L_E(\vec{k})$ when $n_2 \rightarrow 0$; then I will derive the limiting form of the functions $\vec{\phi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2)$. This will lead immediately to the conclusion stated at the end of this subsection.

When $n_2 \rightarrow 0$, it is easy, from (2.35) and (2.49), and from (2.87), (2.88) and (2.85), to verify that:

$$\begin{aligned} \bar{\Lambda}_{\vec{k}}^{(1,1)} &= \bar{\Lambda}_{\vec{k},1} ; & \bar{\Lambda}_{\vec{k}}^{(1,2)} &= \bar{\Lambda}_{\vec{k},1}^{(2,1)} = 0 \\ \Lambda_{\vec{k}}^{(2,2)} &= {}^{(1)}\Lambda^{(2,2)} = n_1 \chi_{12} \sigma_{12}^2 \int d\sigma d\vec{v}_3 {}^{(1)}\phi_0^{(1)}(\vec{v}_3^{(1)}) |\vec{v}_{23}^{(2,1)} \cdot \hat{\sigma}| \times \\ &\times \theta(\vec{v}_{23}^{(2,1)} \cdot \hat{\sigma}) [b_{23}^{(2,1)}(\hat{\sigma}) - 1] \end{aligned} \quad (2.108)$$

$$\bar{\Lambda}_{\vec{k}}^{(2,2)} f(\vec{v}_2) = {}^{(1)}\Lambda^{(2,2)} f(\vec{v}_2) - \int d\vec{v}_2 \phi_0(\vec{v}_2) {}^{(1)}\Lambda^{(2,2)} f(\vec{v}_2) = {}^{(1)}\bar{\Lambda}^{(2,2)}$$

Next, using (1.10) and (1.18), it follows that when $n_2=0$ we have $S_{11}(k)=S(k)$, $S_{12}(k)=S_{21}(k)=0$ and $S_{22}(k)=1$, where $S(k)$ is the simple fluid static structure factor. Therefore, for the factors $m^{(i,j)}(k)$ involved in the mean field term $A_{\vec{k}}^{(i,j)}$ in (2.89), we find, from (2.82), (2.90) and (2.91):

$$m^{(1,1)}(k) = \frac{ik}{\sqrt{\beta m_1}} \left(1 - \frac{1}{\sqrt{S(k)}} \right)$$

$$m^{(1,2)}(k) = m^{(2,1)}(k) = m^{(2,2)}(k) = 0 \quad (2.109)$$

Combining (2.108), (2.109), (2.83), and the definition of $A_{\vec{k},1}$ in (2.50), we obtain:

$$L_E^{(1,1)}(\vec{k}) = -ikv_{1z} + \bar{\Lambda}_{\vec{k},1} + A_{\vec{k},1} = L_{E,1}(\vec{k})$$

$$L_E^{(2,2)}(\vec{k}) = -ikv_{2z} + {}^{(1)}\bar{\Lambda}^{(2,2)}; \quad L_E^{(1,2)}(\vec{k}) = L_E^{(2,1)}(\vec{k}) = 0 \quad (2.110)$$

Besides, the functions $\vec{\phi}_1^{(1)}(\vec{v}_1, \vec{v}_2; k)$ and $\vec{\phi}_1^{(2)}(\vec{v}_1, \vec{v}_2; k)$ in (2.81) reduce to:

$$\vec{\phi}_1^{(1)}(\vec{v}_1, \vec{v}_2; k) = \sqrt{S(k)} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\vec{\phi}_1^{(2)}(\vec{v}_1, \vec{v}_2; k) = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (2.111)$$

while the other $\vec{\phi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2)$, for $\ell \neq 1$, are still given by (2.80):

$$\vec{\phi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2) = \vec{\psi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2); \quad \ell \neq 1 \quad (2.112)$$

Comparing (2.110), (2.111), (2.112) and (2.20) we see that the dynamics is now divided into two independent parts. One reproduces exactly the kinetic theory of a simple fluid of particles of species 1, which will give the correlation functions (2.18). The other part, represented by $L_E^{(2,2)}(\vec{k})$, describes the dynamics of particles of species 2 with a collision operator ${}^{(1)}\Lambda^{(2,2)}$ that takes into account only the collisions with particles of species 1; thus it can be interpreted as the dynamics of a single particle of species 2 imbedded in the simple fluid of particles of species 1.

2.4.2 The case $\sigma_1 = \sigma_2 = \sigma$ and $m_1 = m_2 = m$

The proof of the reduction to the simple fluid dynamics is, in this case, more elaborate. But as a reward we get something new and very

interesting, because we obtain not only the simple fluid correlation functions (2.18), that I write again here:

$$F_{\ell m}^E(k, t) = \langle \phi_{\ell}(\vec{v}_1), e^{tL_{E,1}(\vec{k})} \phi_m(\vec{v}_1) \rangle_1 \quad (2.113)$$

(which are the kinetic approximations for the exact expressions (2.11)), but also the simple fluid self correlation functions, which I will define shortly, and that are the analogous of the self intermediate scattering function (1.23). As mentioned in the introduction of this section, in the usual kinetic theory of simple fluids, a separate calculation is necessary to obtain the correlation functions (2.113) and the self correlation functions.

Before proceeding to the proof, I introduce these self correlation functions, and explain how they are computed in the usual kinetic theory of simple fluids. They are defined by:

$$F_{\ell m}^S(k, t) = \langle \psi_{\ell}(\vec{v}_1) e^{i\vec{k} \cdot \vec{r}_1} e^{tL_1} \psi_m(\vec{v}_1) e^{-i\vec{k} \cdot \vec{r}_1} \rangle_N \quad (2.114)$$

where ψ_{ℓ} 's are the same functions (2.16) (I am always taking \vec{k} parallel to the z-axis), and the right-hand side does not depend on the choice of the particle (here particle 1). The initial values of the $F_{\ell m}^S(k, t)$ are:

$$F_{\ell m}^S(k, 0) = \delta_{\ell m} \quad (2.115)$$

Following a procedure completely analogous to that of subsection 2.1.2, in kinetic theory one approximates these functions by:

$$F_{\ell m}^S(k, t) = \langle \psi_{\ell}(\vec{v}_1), e^{tL_{E,1}^S(\vec{k})} \psi_m(\vec{v}_1) \rangle_1 \quad (2.116)$$

Here the kinetic operator $L_{E,1}^S(\vec{k})$ is given by:

$$L_{E,1}^S(\vec{k}) = -ikv_{1z} + \Lambda_1^S \quad (2.117)$$

where the self collision operator is:

$$\Lambda_1^S = n\chi\sigma^2 \int d\hat{\sigma} d\vec{v}_2 \phi_0(\vec{v}_2) |\vec{v}_{12} \cdot \hat{\sigma}| \theta(\vec{v}_{12} \cdot \hat{\sigma}) [b_{12}(\hat{\sigma}) - 1] \quad (2.118)$$

which is identical to (2.32). As we have seen in section 2.1, this expression plus (2.35) constitute the simple fluid collision operator $\Lambda_{\vec{k},1}$; disregarding for a moment that the real collision operator is $\bar{\Lambda}_{\vec{k},1}$, defined in (2.49) (I will show below that in the matrix representation only one matrix element is different between $\Lambda_{\vec{k},1}$ and $\bar{\Lambda}_{\vec{k},1}$), one could say that the self collision operator Λ_1^S is "half" of the full collision operator $\Lambda_{\vec{k},1}$.

In order to show that, in our binary mixture kinetic theory, we get both (2.113) and (2.116) of simple fluids, when we put $\sigma_1 = \sigma_2 = \sigma$ and $m_1 = m_2 = m$, I will construct two suitable linear combinations of the functions $\vec{\phi}_\ell^{(1)}$ and $\vec{\phi}_\ell^{(2)}$ for each ℓ (the $\vec{\phi}_\ell^{(i)}$ are defined in (2.78), (2.80) and (2.81)). Therefore the matrix representation of the operator $L_E(\vec{k})$ will change. The point of the proof will be to show that, regardless of the values of x_1 and $x_2 = 1 - x_1$ this transformed matrix of $L_E(\vec{k})$ is divided in two blocks, one with the matrix elements of $L_{E,1}(\vec{k})$, and the other with those of $L_{E,1}^S(\vec{k})$.

As a first step I will build the linear combinations mentioned above, then, as a second step, I will compute the transformed matrix of $L_E(\vec{k})$. The two steps will be separated using roman numbers. In turn, step II will consist of different steps, separated using latin characters.

I. The two linear combinations of $\vec{\phi}_\ell^{(1)}$ and $\vec{\phi}_\ell^{(2)}$

To build the needed two linear combinations of $\vec{\phi}_\ell^{(1)}$ and $\vec{\phi}_\ell^{(2)}$, I start constructing two linear combinations of the dynamical variables $a_\ell^{(1)}$ and

$a_\ell^{(2)}$, defined in (2.70). The combinations for $\vec{\phi}_\ell^{(1)}$ and $\vec{\phi}_\ell^{(2)}$ will then follow automatically from our kinetic representation of the correlation functions (2.79).

Comparing the definitions (2.10) and (2.70) for a_ℓ and $a_\ell^{(i)}$, and the definitions (2.11) and (2.69) for $F_{\ell m}$ and $F_{\ell m}^{(i,j)}$, we see that, when the two components are the same, we have:

$$F_{\ell m}(k, t) = x_1 F_{\ell m}^{(1,1)}(k, t) + x_2 F_{\ell m}^{(2,2)}(k, t) + 2\sqrt{x_1 x_2} F_{\ell m}^{(1,2)}(k, t) \quad (2.119)$$

This same expression is obtained writing:

$$F_{\ell m}(k, t) = \langle a_\ell'^* (\vec{k}, \Gamma) e^{tL} a_m' (\vec{k}, \Gamma) \rangle_N \quad (2.120)$$

if I define:

$$a_\ell'(\vec{k}, \Gamma) = \sqrt{x_1} a_\ell^{(1)}(\vec{k}, \Gamma) + \sqrt{x_2} a_\ell^{(2)}(\vec{k}, \Gamma) = \frac{1}{\sqrt{N}} \sum_{p=1}^N \psi_\ell(\vec{v}_p) e^{-i\vec{k} \cdot \vec{r}_p} \quad (2.121)$$

The other linear combination of $a_\ell^{(1)}$ and $a_\ell^{(2)}$ will be denoted by $a_\ell''(\vec{k}, \Gamma)$. I claim that, if I define:

$$a_\ell''(\vec{k}, \Gamma) = \sqrt{x_2} a_\ell^{(1)}(\vec{k}, \Gamma) - \sqrt{x_1} a_\ell^{(2)}(\vec{k}, \Gamma) \quad (2.122)$$

then:

$$\langle a_\ell'^* (\vec{k}, \Gamma) e^{tL} a_m' (\vec{k}, \Gamma) \rangle_N = \langle a_m'^* (\vec{k}, \Gamma) e^{tL} a_\ell''(\vec{k}, \Gamma) \rangle_N = 0 \quad (2.123)$$

In order to show this I have to use the following property of the $F_{\ell m}(k, t)$ (expressed by (2.124) and (2.125)). Since the hamiltonian and the (pseudo)-Liouville operator are invariant with respect to the interchange of any two particles, we have:

$$\begin{aligned} F_{\ell m}(k, t) &= \frac{1}{N} \left\langle \sum_{p=1}^N \psi_\ell(\vec{v}_p) e^{i\vec{k} \cdot \vec{r}_p} e^{tL} \sum_{q=1}^N \psi_m(\vec{v}_q) e^{-i\vec{k} \cdot \vec{r}_q} \right\rangle_N = \\ &= F_{\ell m}^s(k, t) + F_{\ell m}^d(k, t) \end{aligned} \quad (2.124)$$

where $F_{\ell m}^s(k, t)$ is defined by (2.114) and:

$$F_{\ell m}^d(k, t) = (N-1) \langle \psi_\ell(\vec{v}_1) e^{i\vec{k} \cdot \vec{r}_1} e^{tL} \psi_m(\vec{v}_2) e^{-i\vec{k} \cdot \vec{r}_2} \rangle_N \quad (2.125)$$

From this, and remembering that the sums in the definitions of $a_\ell^{(1)}$ and $a_\ell^{(2)}$ run over two disjoint set of, respectively, N_1 and N_2 particles, with $N=N_1+N_2$, one obtains, after some manipulations:

$$\langle a_\ell^{*}(\vec{k},\Gamma) e^{tL} a'_m(\vec{k},\Gamma) \rangle_N = 0 \quad (2.126)$$

In a similar fashion, one can also prove that:

$$\langle a_\ell^{*}(\vec{k},\Gamma) e^{tL} a''_m(\vec{k},\Gamma) \rangle_N = F_{\ell m}^S(k,t) \quad (2.127)$$

Actually one obtains:

$$\langle a_\ell^{*}(\vec{k},\Gamma) e^{tL} a''_m(\vec{k},\Gamma) \rangle_N = F_{\ell m}^S(k,t) - F_{\ell m}^d(k,t)/(N-1) \quad (2.128)$$

But since $F_{\ell m}$ and $F_{\ell m}^S$ are of order one, and so is $F_{\ell m}^d$, and since N is an extremely large number, one can neglect the second term on the right-hand side of (2.128), so that one obtains (2.127).

Since each $a_\ell^{(i)}(\vec{k},\Gamma)$ is associated with the two component function $\vec{\phi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2)$, also each $a'_\ell(\vec{k},\Gamma)$ and $a''_\ell(\vec{k},\Gamma)$ will be associated with a two component function. More precisely, according to (2.121) and (2.122) I build the two linear combinations:

$$\begin{aligned} \vec{\phi}'_\ell(\vec{v}_1, \vec{v}_2) &= \sqrt{x_1} \vec{\phi}_\ell^{(1)}(\vec{v}_1, \vec{v}_2) + \sqrt{x_2} \vec{\phi}_\ell^{(2)}(\vec{v}_1, \vec{v}_2) \\ \vec{\phi}''_\ell(\vec{v}_1, \vec{v}_2) &= \sqrt{x_2} \vec{\phi}_\ell^{(1)}(\vec{v}_1, \vec{v}_2) - \sqrt{x_1} \vec{\phi}_\ell^{(2)}(\vec{v}_1, \vec{v}_2) \end{aligned} \quad (2.129)$$

II. The transformed matrix of $L_E(\vec{k})$

I will now prove the following four equalities, which show that our kinetic theory reproduces correctly the simple fluid when the two components are equal, and in addition gives the (kinetic approximation of the) $F_{\ell m}^S(k,t)$:

$$\begin{aligned}
 <<\phi'_\ell(\vec{v}_1, \vec{v}_2), e^{tL_E(\vec{k})} \phi'_m(\vec{v}_1, \vec{v}_2)>_1>_2 = F_{\ell m}^E(k, t) \\
 <<\phi''_\ell(\vec{v}_1, \vec{v}_2), e^{tL_E(\vec{k})} \phi''_m(\vec{v}_1, \vec{v}_2)>_1>_2 = F_{\ell m}^{SE}(k, t) \quad (2.130) \\
 <<\phi'_\ell(\vec{v}_1, \vec{v}_2), e^{tL_E(\vec{k})} \phi''_m(\vec{v}_1, \vec{v}_2)>_1>_2 = <<\phi''_m(\vec{v}_1, \vec{v}_2), e^{tL_E(\vec{k})} \phi'_\ell(\vec{v}_1, \vec{v}_2)>_1>_2 = 0
 \end{aligned}$$

This will be accomplished in the following steps: a) I will prove that the set of functions $\vec{\phi}'_\ell, \vec{\phi}''_\ell$ ($\ell=1,2,\dots$) is orthogonal; b) I will show that only $\vec{\phi}'_1$ is not of unit norm, its norm being $S(k)$; c) I will build the matrix representation of $L_E(\vec{k})$ for the orthonormal set $\vec{\psi}'_\ell, \vec{\psi}''_\ell$ obtained from $\vec{\phi}'_\ell, \vec{\phi}''_\ell$ (so that actually the only difference is that between $\vec{\psi}'_1$ and $\vec{\phi}'_1$), and then the equalities (2.130) will be finally proved showing that:

$$\begin{aligned}
 <<\vec{\psi}'_\ell(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}'_m(\vec{v}_1, \vec{v}_2)>_1>_2 &= <\psi_\ell(\vec{v}_1), L_{E,1}(\vec{k}) \psi_m(\vec{v}_1)>_1 \\
 <<\vec{\psi}''_\ell(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}''_m(\vec{v}_1, \vec{v}_2)>_1>_2 &= <\psi_\ell(\vec{v}_1), L_{E,1}^S(\vec{k}) \psi_m(\vec{v}_1)>_1 \quad (2.131) \\
 <<\vec{\psi}'_\ell(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}''_m(\vec{v}_1, \vec{v}_2)>_1>_2 &= <<\vec{\psi}''_m(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}'_\ell(\vec{v}_1, \vec{v}_2)>_1>_2 = 0
 \end{aligned}$$

a)

First I have to find $\vec{\phi}'_\ell$ and $\vec{\phi}''_\ell$ in terms of the $\vec{\psi}_\ell^{(i)}$, defined by (2.78), since the matrix representation of $L_E(\vec{k})$ has been built for that orthonormal set. From (2.80), which shows that $\vec{\phi}_\ell^{(i)} = \vec{\psi}_\ell^{(i)}$ for $\ell \geq 2$, we have that:

$$\begin{aligned}
 \vec{\phi}'_\ell(\vec{v}_1, \vec{v}_2) &= \sqrt{x_1} \vec{\psi}_\ell^{(1)}(\vec{v}_1, \vec{v}_2) + \sqrt{x_2} \vec{\psi}_\ell^{(2)}(\vec{v}_1, \vec{v}_2) \\
 \vec{\phi}''_\ell(\vec{v}_1, \vec{v}_2) &= \sqrt{x_2} \vec{\psi}_\ell^{(1)}(\vec{v}_1, \vec{v}_2) - \sqrt{x_1} \vec{\psi}_\ell^{(2)}(\vec{v}_1, \vec{v}_2) \quad (2.132)
 \end{aligned}$$

For $\ell=1$ I have to use the relations (2.81) between $\vec{\phi}_1^{(1)}, \vec{\phi}_1^{(2)}$ and $\vec{\psi}_1^{(1)}, \vec{\psi}_1^{(2)}$. Then it follows that:

$$\begin{aligned}
 \vec{\phi}'_1(\vec{v}_1, \vec{v}_2; k) &= \left(\sqrt{x_1 S_{11}(k)} \cos \alpha(k) + \sqrt{x_2 S_{22}(k)} \sin \alpha(k) \right) \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2) + \\
 &+ \left(\sqrt{x_1 S_{11}(k)} \sin \alpha(k) + \sqrt{x_2 S_{22}(k)} \cos \alpha(k) \right) \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2) \\
 \vec{\phi}''_1(\vec{v}_1, \vec{v}_2; k) &= \left(\sqrt{x_2 S_{11}(k)} \cos \alpha(k) - \sqrt{x_1 S_{22}(k)} \sin \alpha(k) \right) \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2) + \\
 &+ \left(\sqrt{x_2 S_{11}(k)} \sin \alpha(k) - \sqrt{x_1 S_{22}(k)} \cos \alpha(k) \right) \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2) \quad (2.133)
 \end{aligned}$$

Since $\vec{\psi}_\ell^{(1)}$ and $\vec{\psi}_\ell^{(2)}$ are an orthonormal set, it follows immediately from (2.132) and (2.133) that, for $(\ell, m) \neq (1, 1)$:

$$\begin{aligned}
 \langle \langle \vec{\phi}'_\ell(\vec{v}_1, \vec{v}_2), \vec{\phi}'_m(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 &= \langle \langle \vec{\phi}''_\ell(\vec{v}_1, \vec{v}_2), \vec{\phi}''_m(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \delta_{\ell m} \\
 \langle \langle \vec{\phi}'_\ell(\vec{v}_1, \vec{v}_2), \vec{\phi}''_m(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 &= 0 \quad (2.134)
 \end{aligned}$$

b)

In order to compute the scalar products involving $\vec{\phi}'_1$ and $\vec{\phi}''_1$ I need first the following relations. Since in a simple fluid which has been artificially divided in two components all $g_{ij}(r)$ (cf. (1.16)) are equal, it follows from (1.10) and (1.18) that:

$$\begin{aligned}
 S_{11}(k) &= x_1 S(k) + x_2 \\
 S_{22}(k) &= x_2 S(k) + x_1 \\
 S_{12}(k) &= \sqrt{x_1 x_2} (S(k) - 1) \quad (2.135)
 \end{aligned}$$

from which one can derive:

$$S_{11}(k) S_{22}(k) - S_{12}^2(k) = S(k) \quad (2.136)$$

Using (2.135), (2.136) and the definition (2.82) of $\alpha(k)$, one obtains, from a tedious but straightforward calculation:

$$\begin{aligned}
 \langle \langle \vec{\phi}'_1(\vec{v}_1, \vec{v}_2; k), \vec{\phi}'_1(\vec{v}_1, \vec{v}_2; k) \rangle_1 \rangle_2 &= S(k) \\
 \langle \langle \vec{\phi}''_1(\vec{v}_1, \vec{v}_2; k), \vec{\phi}''_1(\vec{v}_1, \vec{v}_2; k) \rangle_1 \rangle_2 &= 1 \\
 \langle \langle \vec{\phi}'_1(\vec{v}_1, \vec{v}_2; k), \vec{\phi}''_1(\vec{v}_1, \vec{v}_2; k) \rangle_1 \rangle_2 &= 0 \quad (2.137)
 \end{aligned}$$

c)

Using (2.134) and (2.135) the orthonormal set $\vec{\psi}'_\ell, \vec{\psi}''_\ell$ is given by:

$$\begin{aligned}\vec{\psi}'_1(\vec{v}_1, \vec{v}_2; k) &= \frac{1}{\sqrt{S(k)}} \vec{\phi}'_1(\vec{v}_1, \vec{v}_2; k); & \vec{\psi}''_1(\vec{v}_1, \vec{v}_2; k) &= \vec{\phi}''_1(\vec{v}_1, \vec{v}_2; k); \\ \vec{\psi}'_\ell(\vec{v}_1, \vec{v}_2) &= \vec{\phi}'_\ell(\vec{v}_1, \vec{v}_2) \quad \text{and} \quad \vec{\psi}''_\ell(\vec{v}_1, \vec{v}_2) = \vec{\phi}''_\ell(\vec{v}_1, \vec{v}_2) \quad \ell \neq 1\end{aligned}\quad (2.138)$$

Next I proceed to the matrix representation of $L_E(\vec{k})$ in this orthonormal set and to the proof of the equalities (2.131). A convenient way to do this is to separate the contributions to the matrix elements of $L_E(\vec{k})$, $L_{E,1}(\vec{k})$ and $L_{E,1}^S(\vec{k})$ that come from the free streaming, the collision operator and the mean field term, respectively. It will only be necessary to indicate formally (i. e., with symbols) the various terms. I will begin with $L_{E,1}(\vec{k})$.

Before I do so, I first show a property which is used in the formal manipulation that I will make, and which is also useful in the computation of the matrix elements of the operator $L_E(\vec{k})$, treated in the next chapter. The property is that the operators $\Lambda_{\vec{k},1}$ and $\bar{\Lambda}_{\vec{k},1}$, related by (2.49), that I rewrite here:

$$\bar{\Lambda}_{\vec{k}} f(\vec{v}_1) = \Lambda_{\vec{k}} f(\vec{v}_1) - \langle \Lambda_{\vec{k}} f(\vec{v}_1) \rangle_1 \quad (2.139)$$

differ only in the matrix element (1,2). In fact, since $\Lambda_{\vec{k},1} \psi_1(\vec{v}_1) = 0$, we have, first of all, that:

$$\langle \psi_\ell(\vec{v}_1), \bar{\Lambda}_{\vec{k},1} \psi_1(\vec{v}_1) \rangle_1 = \langle \psi_\ell(\vec{v}_1), \Lambda_{\vec{k},1} \psi_1(\vec{v}_1) \rangle_1 = 0 \quad (2.140)$$

Then since the second term on the right-hand side of (2.139) is proportional to $\psi_1(\vec{v}_1)$, we also have that:

$$\langle \psi_\ell(\vec{v}_1), \bar{\Lambda}_{\vec{k},1} \psi_m(\vec{v}_1) \rangle_1 = \langle \psi_\ell(\vec{v}_1), \Lambda_{\vec{k},1} \psi_m(\vec{v}_1) \rangle_1 \quad \ell, m = 2, 3, \dots \quad (2.141)$$

Therefore the difference between the matrix elements of $\bar{\Lambda}_{\vec{k},1}$ and $\Lambda_{\vec{k},1}$ can only come from the matrix elements:

$$\langle \psi_1(\vec{v}_1), \bar{\Lambda}_{\vec{k},1} \psi_\ell(\vec{v}_1) \rangle_1, \quad \langle \psi_1(\vec{v}_1), \Lambda_{\vec{k},1} \psi_\ell(\vec{v}_1) \rangle_1 \quad \ell = 2, 3, \dots \quad (2.142)$$

From the definition (2.139) of $\bar{\Lambda}_{\vec{k}}$ it follows that:

$$\langle \psi_1(\vec{v}_1), \bar{\Lambda}_{\vec{k},1} \psi_\ell(\vec{v}_1) \rangle_1 = 0 \quad \ell=2,3,\dots \quad (2.143)$$

To compute the second set of matrix elements in (2.142) I use that the transpose of $\Lambda_{\vec{k},1}$ can be shown to be¹²⁾:

$$\Lambda_{\vec{k},1}^T = \Lambda_{\vec{k},1} - \text{in} \chi \sigma^2 4\pi j_1(k\sigma) \frac{1}{\sqrt{\beta_m}} \left(|\psi_2(\vec{v}_1)\rangle_1 \langle \psi_1(\vec{v}_1)| - |\psi_1(\vec{v}_1)\rangle_1 \langle \psi_2(\vec{v}_1)| \right) \quad (2.144)$$

where $j_1(x)$ is the spherical Bessel function of index 1. Therefore:

$$\langle \psi_1(\vec{v}_1), \Lambda_{\vec{k},1} \psi_\ell(\vec{v}_1) \rangle_1 = \langle \psi_\ell(\vec{v}_1), \Lambda_{\vec{k},1} \psi_1(\vec{v}_1) \rangle_1 = \text{in} \chi \sigma^2 4\pi j_1(k\sigma) \frac{1}{\sqrt{\beta_m}} \delta_{\ell 2} \quad (2.145)$$

thus proving that $\Lambda_{\vec{k},1}$ and $\bar{\Lambda}_{\vec{k},1}$ differ only in the (1,2) matrix element. I

have also shown that $\bar{\Lambda}_{\vec{k},1}$ has vanishing matrix elements $\langle \psi_\ell(\vec{v}_1), \bar{\Lambda}_{\vec{k},1} \psi_m(\vec{v}_1) \rangle_1$

when ℓ and/or m is equal 1 (cf. (2.141) and (2.143)), and that in computing

the non vanishing matrix elements, with $\ell, m \neq 1$, one can replace $\bar{\Lambda}_{\vec{k},1}$ with

$\Lambda_{\vec{k},1}$. In a completely similar manner it is shown that the matrix elements:

$$\langle \langle \vec{\psi}_\ell^{(i)}(\vec{v}_1, \vec{v}_2), \bar{\Lambda}_{\vec{k}} \vec{\psi}_m^{(j)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 \quad (2.146)$$

of the binary mixture collision operator $\bar{\Lambda}_{\vec{k}}$, vanish when ℓ and/or m is equal

1, and that when $\ell, m \neq 1$ we can replace $\bar{\Lambda}_{\vec{k}}$ with $\Lambda_{\vec{k}}$ [4]. This property is also

used in the computation of the matrix elements in the next chapter.

Now I proceed, as mentioned above, to the separation of the different contributions to the matrix elements of $L_{E,1}(\vec{k})$. I begin with the matrix elements with $\ell, m \neq 1$. For those the contribution comes from the free

streaming and the collision operator, while the mean field operator does not contribute. I formally indicate, for $\ell, m \neq 1$:

$$\begin{aligned} \langle \psi_\ell(\vec{v}_1), (-ikv_{1z}) \psi_m(\vec{v}_1) \rangle_1 &= c_{\ell m} \\ \langle \psi_\ell(\vec{v}_1), \Lambda_{\vec{k},1} \psi_m(\vec{v}_1) \rangle_1 &= a_{\ell m} + b_{\ell m} \quad \ell, m \neq 1 \end{aligned} \quad (2.147)$$

where $a_{\ell m}$ and $b_{\ell m}$ correspond, respectively, to the separation of $\Lambda_{\vec{k},1}$ in the two pieces (2.32) and (2.35). Next I consider the matrix elements where ℓ and/or m is equal to 1. The mean field operator $\Lambda_{\vec{k},1}$ has only the elements (1,2) and (2,1), as follows from (2.50), which are both equal to:

$$\frac{ik}{\sqrt{\beta m}} \left(1 - \frac{1}{\sqrt{S(k)}} \right) \quad (2.148)$$

Also, among the matrix elements of the free streaming operator that involve $\psi_1(\vec{v}_1)$, only the (1,2) and (2,1) elements are different from zero, and they are given by:

$$\langle \psi_1(\vec{v}_1), (-ikv_{1z}) \psi_2(\vec{v}_1) \rangle_1 = \langle \psi_2(\vec{v}_1), (-ikv_{1z}) \psi_1(\vec{v}_1) \rangle_1 = -\frac{ik}{\sqrt{\beta m}} \quad (2.149)$$

which, combined with (2.148), gives:

$$\begin{aligned} \langle \psi_1(\vec{v}_1), (-ikv_{1z} + \Lambda_{\vec{k},1}) \psi_2(\vec{v}_1) \rangle_1 &= \langle \psi_2(\vec{v}_1), (-ikv_{1z} + \Lambda_{\vec{k},1}) \psi_1(\vec{v}_1) \rangle_1 = \\ &= -\frac{ik}{\sqrt{\beta m S(k)}} \end{aligned} \quad (2.150)$$

Next I apply the same separation procedure to $L_{E,1}^S(\vec{k})$, defined in (2.117) and (2.118). The free streaming term has obviously the same matrix elements of $L_{E,1}(\vec{k})$; also, it follows from (2.117) and (2.118) that the collision operator Λ_1^S has elements:

$$\langle \psi_\ell(\vec{v}_1), \Lambda_1^S \psi_m(\vec{v}_1) \rangle_1 = a_{\ell m} \quad \ell, m \neq 1 \quad (2.151)$$

and all the matrix elements of Λ_1^S with ℓ and/or m equal to 1 vanish.

With this I have formally computed the matrix elements on the right-hand sides of the first and second expressions in (2.131). To compute also

the left-hand sides I make the same formal evaluation for the binary mixture kinetic operator $L_E(\vec{k})$. Here also I begin with the case $\ell, m \neq 1$.

From the structure of $L_E(\vec{k})$, shown in (2.83), one can obtain the following results, when the two components are the same. For the free streaming the matrix elements are:

$$\begin{aligned} & \langle \langle \vec{\psi}_\ell^{(1)}(\vec{v}_1, \vec{v}_2), (-ikv_{1z}) \vec{\psi}_m^{(1)}(v_1, v_2) \rangle_1 \rangle_2 = \\ & = \langle \langle \vec{\psi}_\ell^{(2)}(\vec{v}_1, \vec{v}_2), (-ikv_{2z}) \vec{\psi}_m^{(2)}(v_1, v_2) \rangle_1 \rangle_2 = c_{\ell m} \quad \ell, m \neq 1 \end{aligned} \quad (2.152)$$

while the elements involving $\vec{\psi}_\ell^{(i)}$ and $\vec{\psi}_m^{(j)}$ with $i \neq j$ vanish. For the collision operator we have:

$$\begin{aligned} & \langle \langle \vec{\psi}_\ell^{(1)}(\vec{v}_1, \vec{v}_2), \Lambda_{\vec{k}} \vec{\psi}_m^{(1)}(v_1, v_2) \rangle_1 \rangle_2 = a_{\ell m} + x_1 b_{\ell m} \\ & \langle \langle \vec{\psi}_\ell^{(2)}(\vec{v}_1, \vec{v}_2), \Lambda_{\vec{k}} \vec{\psi}_m^{(2)}(v_1, v_2) \rangle_1 \rangle_2 = a_{\ell m} + x_2 b_{\ell m} \\ & \langle \langle \vec{\psi}_\ell^{(1)}(\vec{v}_1, \vec{v}_2), \Lambda_{\vec{k}} \vec{\psi}_m^{(2)}(v_1, v_2) \rangle_1 \rangle_2 = \langle \langle \vec{\psi}_\ell^{(2)}(\vec{v}_1, \vec{v}_2), \Lambda_{\vec{k}} \vec{\psi}_m^{(1)}(v_1, v_2) \rangle_1 \rangle_2 = \\ & = \sqrt{x_1 x_2} b_{\ell m} \quad \ell, m \neq 1 \end{aligned} \quad (2.153)$$

Like for $L_{E,1}(\vec{k})$, the mean field operator does not contribute when $\ell, m \neq 1$. Now I can prove the equalities (2.131) for $\ell, m \neq 1$. From the definitions (2.138) and (2.129), we have, using (2.152) and (2.153):

$$\begin{aligned} & \langle \langle \vec{\psi}_\ell'(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}_m'(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = x_1 (c_{\ell m} + a_{\ell m} + x_1 b_{\ell m}) + x_2 (c_{\ell m} + a_{\ell m} + x_2 b_{\ell m}) + \\ & + 2\sqrt{x_1 x_2} \sqrt{x_1 x_2} b_{\ell m} = c_{\ell m} + a_{\ell m} + b_{\ell m} \end{aligned} \quad (2.154)$$

which is equal to the right-hand side of the first expression in (2.131).

Then:

$$\begin{aligned} & \langle \langle \vec{\psi}_\ell''(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}_m''(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = x_2 (c_{\ell m} + a_{\ell m} + x_1 b_{\ell m}) + x_1 (c_{\ell m} + a_{\ell m} + x_2 b_{\ell m}) + \\ & - 2\sqrt{x_1 x_2} \sqrt{x_1 x_2} b_{\ell m} = c_{\ell m} + a_{\ell m} \end{aligned} \quad (2.155)$$

which is equal to the right-hand side of the second expression in (2.131).

Finally:

$$\begin{aligned}
 & \langle \langle \vec{\psi}'_{\ell}(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}_m(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \langle \langle \vec{\psi}_m(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}'_{\ell}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 & = \sqrt{x_1 x_2} (c_{\ell m} + a_{\ell m} + x_1 b_{\ell m}) - \sqrt{x_1 x_2} (c_{\ell m} + a_{\ell m} + x_2 b_{\ell m}) + (x_2 - x_1) \sqrt{x_1 x_2} b_{\ell m} = 0 \quad (2.156)
 \end{aligned}$$

thus proving the last expression in (2.131) for $\ell, m \neq 1$.

It remains to prove the equalities in (2.131) for the case in which ℓ or m is equal 1. The only non vanishing matrix elements of the mean field operator are:

$$\begin{aligned}
 & \langle \langle \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_2^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \langle \langle \vec{\psi}_2^{(1)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 & = \frac{ik}{\sqrt{\beta m}} \left[1 - \sqrt{\frac{S_{22}(k)}{S(k)}} \cos \alpha(k) \right] \\
 & \langle \langle \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_2^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \langle \langle \vec{\psi}_2^{(2)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 & = \frac{ik}{\sqrt{\beta m}} \sqrt{\frac{S_{11}(k)}{S(k)}} \sin \alpha(k) \\
 & \langle \langle \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_2^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \langle \langle \vec{\psi}_2^{(1)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 & = \frac{ik}{\sqrt{\beta m}} \sqrt{\frac{S_{22}(k)}{S(k)}} \sin \alpha(k) \\
 & \langle \langle \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_2^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \langle \langle \vec{\psi}_2^{(2)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 & = \frac{ik}{\sqrt{\beta m}} \left[1 - \sqrt{\frac{S_{11}(k)}{S(k)}} \cos \alpha(k) \right] \quad (2.157)
 \end{aligned}$$

Also the matrix elements of the free streaming, when ℓ or m is equal to 1, involve only the elements with $\ell=1, m=2$ and $\ell=2, m=1$. They are all equal to:

$$- \frac{ik}{\sqrt{\beta m}} \quad (2.158)$$

Therefore, from the definitions (2.138) and (2.129), and using (2.157), (2.158), and (2.136), we find, after some manipulations:

$$\begin{aligned}
 & \langle \langle \vec{\psi}'_1(\vec{v}_1, \vec{v}_2; k), L_E(\vec{k}) \vec{\psi}'_2(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \langle \langle \vec{\psi}'_2(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}'_1(\vec{v}_1, \vec{v}_2; k) \rangle_1 \rangle_2 = \\
 & = \frac{ik}{\sqrt{\beta m S(k)}} \quad (2.159)
 \end{aligned}$$

This expression is identical to (2.150), thus completing the proof of the first equality in (2.131). The proof of the second and third equalities is completed in an analogous way by the following expressions:

$$\begin{aligned} \langle \langle \vec{\psi}_1''(\vec{v}_1, \vec{v}_2; k), L_E(\vec{k}) \vec{\psi}_2''(\vec{v}_1, \vec{v}_2) \rangle \rangle_1 \rangle_2 &= \langle \langle \vec{\psi}_2''(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}_1''(\vec{v}_1, \vec{v}_2; k) \rangle \rangle_1 \rangle_2 = \\ &= - \frac{ik}{\sqrt{\beta m}} \end{aligned} \quad (2.160)$$

$$\begin{aligned} \langle \langle \vec{\psi}_1'(\vec{v}_1, \vec{v}_2; k), L_E(\vec{k}) \vec{\psi}_2''(\vec{v}_1, \vec{v}_2) \rangle \rangle_1 \rangle_2 &= \langle \langle \vec{\psi}_2''(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}_1'(\vec{v}_1, \vec{v}_2; k) \rangle \rangle_1 \rangle_2 = \\ = \langle \langle \vec{\psi}_1''(\vec{v}_1, \vec{v}_2; k), L_E(\vec{k}) \vec{\psi}_2'(\vec{v}_1, \vec{v}_2) \rangle \rangle_1 \rangle_2 &= \langle \langle \vec{\psi}_2'(\vec{v}_1, \vec{v}_2), L_E(\vec{k}) \vec{\psi}_1''(\vec{v}_1, \vec{v}_2; k) \rangle \rangle_1 \rangle_2 = 0 \end{aligned}$$

I have therefore completed the proof of: a) the separation of the matrix representation of $L_E(\vec{k})$ in the orthonormal set (2.138) into two blocks, a separation that is expressed by the third equality in (2.131); b) the recovery of the simple fluid correlation functions, when $\sigma_1 = \sigma_2$ and $m_1 = m_2$, with, in addition, c) the possibility to compute the simple fluid self correlation functions. Points b) and c) are contained, respectively, in the first and second equality in (2.131).

Notes

[1] Of course the way of ordering the polynomials is not unique; there are different criteria that one can follow to choose an ordering¹¹⁾; this problem is not of concern in this thesis, since the results are not affected by the choice. In all orderings the first few polynomials are the same.

[2] In binary mixtures in principle one could introduce two constants, $d_1(k)$ and $d_2(k)$; see text below.

[3] The particular form of (2.81) comes from the special role played by $(\ell, m) = (1, 1)$ in the initial values (2.73). Actually, different choices for

$\vec{\phi}_1^{(1)}(\vec{v}_1, \vec{v}_2; k)$ and $\vec{\phi}_1^{(2)}(\vec{v}_1, \vec{v}_2; k)$ are possible, in the sense that one can choose other constant functions depending parametrically on k which satisfy the requirements of our kinetic theory, namely the exact reproduction, at time zero, of the correlation functions and of their first time derivatives. But it can be shown that all the possible choices lead to identical results for the correlation functions.

[4] Similarly to the situation that occurs in simple fluids for $\bar{\Lambda}_{\vec{k},1}$ and

$\Lambda_{\vec{k},1}$, the difference between $\bar{\Lambda}_{\vec{k}}$ and $\Lambda_{\vec{k}}$ comes only from the matrix elements

with $(\ell, m) = (1, 2)$. Here I also note that $\bar{\Lambda}_{\vec{k},1}$ and $\bar{\Lambda}_{\vec{k}}$ are symmetric operators,

while $\Lambda_{\vec{k},1}$ and $\Lambda_{\vec{k}}$ are not symmetric.

The computation

The main purpose of this chapter is to sketch the numerical evaluation of the matrix elements of the kinetic operator $L_E(\vec{k})$ needed in my computation of the $S_{ij}(k, \omega)$. I will also show how the static structure factors $S_{ij}(k)$, which enter some of the matrix elements, are computed. At the end I will mention the phenomenological equation of state which is used to compute the velocity of sound in a hard sphere mixture (or simple fluid); the velocity of sound will be an important quantity in the discussion of my results. This phenomenological equation of state has proved, by molecular dynamics simulations of hard sphere fluids, to be very successful for hard spheres up to high densities.

All the formulas that I have obtained have been evaluated by computer. I should also mention that the zeros of the function $D(k, z)$ (cf. (2.104)), needed in the calculation of the eigenvalues of the the operator $L_E(\vec{k})$, were computed numerically by a computer subroutine.

I will begin with the evaluation of the matrix elements of $L_E(\vec{k})$. As follows from our method of computation, the BGK method, three different types of matrix elements have to be computed: two that concern the kinetic operator $L_E(\vec{k})$, namely the collision operator and the mean field operator (cf. (2.83)), while the third concerns the matrix elements (2.103).

3.1 The matrix elements of the mean field operator

This is the easiest part of the calculation. As is clear from (2.89), there are only 8 non vanishing matrix elements, that are given below:

$$\begin{aligned}
 \langle\langle \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_2^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 &= \langle\langle \vec{\psi}_2^{(1)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 &= \frac{ik}{\sqrt{\beta m_1}} \left[1 - \sqrt{\frac{S_{22}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)}} \cos \alpha(k) \right] \\
 \langle\langle \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_2^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 &= \langle\langle \vec{\psi}_2^{(2)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_1^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 &= \frac{ik}{\sqrt{\beta m_2}} \sqrt{\frac{S_{11}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)}} \sin \alpha(k) \quad (3.1) \\
 \langle\langle \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_2^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 &= \langle\langle \vec{\psi}_2^{(1)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 &= \frac{ik}{\sqrt{\beta m_1}} \sqrt{\frac{S_{22}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)}} \sin \alpha(k) \\
 \langle\langle \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_2^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 &= \langle\langle \vec{\psi}_2^{(2)}(\vec{v}_1, \vec{v}_2), A_{\vec{k}} \vec{\psi}_1^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 &= \frac{ik}{\sqrt{\beta m_2}} \left[1 - \sqrt{\frac{S_{11}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)}} \cos \alpha(k) \right]
 \end{aligned}$$

3.2 The matrix elements of the collision operator

I will give only a few details about the computation of the matrix elements of the collision operator, because the calculations are lengthy and not very enlightening.

As I have noticed in section (2.4), the collision operator $\bar{\Lambda}_{\vec{k}}$ has vanishing matrix elements between $\vec{\psi}_\ell^{(i)}$ and $\vec{\psi}_m^{(j)}$ when ℓ and/or m is equal to

1. In all the other cases, $\bar{\Lambda}_{\vec{k}}$ and $\Lambda_{\vec{k}}$ have the same matrix elements, and the latter can replace the former in the calculations.

To compute the matrix elements of $\Lambda_{\vec{k}}$ for $\ell, m \neq 1$ it is convenient to write them in the following form, using the "elements" $\Lambda_{\vec{k}}^{(i,j)}$ of $\Lambda_{\vec{k}}$, and their subdivision in $^{(1)}\Lambda^{(i,i)}$ and $^{(2)}\Lambda_{\vec{k}}^{(i,j)}$ given by (2.87) and (2.88) ($^{(1)}\Lambda$ has only diagonal "elements"):

$$\begin{aligned}
 & \langle \langle \vec{\psi}_{\ell}^{(1)}(\vec{v}_1, \vec{v}_2), \Lambda_{\vec{k}} \vec{\psi}_m^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 & = \langle \psi_{\ell}^{(1)}(\vec{v}_1), ^{(1)}\Lambda^{(1,1)} \psi_m^{(1)}(\vec{v}_1) \rangle_1 + \langle \psi_{\ell}^{(1)}(\vec{v}_1), ^{(2)}\Lambda_{\vec{k}}^{(1,1)} \psi_m^{(1)}(\vec{v}_1) \rangle_1 \\
 & \langle \langle \vec{\psi}_{\ell}^{(1)}(\vec{v}_1, \vec{v}_2), \Lambda_{\vec{k}} \vec{\psi}_m^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \langle \psi_{\ell}^{(1)}(\vec{v}_1), ^{(2)}\Lambda_{\vec{k}}^{(1,2)} \psi_m^{(2)}(\vec{v}_2) \rangle_1 \quad (3.2) \\
 & \langle \langle \vec{\psi}_{\ell}^{(2)}(\vec{v}_1, \vec{v}_2), \Lambda_{\vec{k}} \vec{\psi}_m^{(1)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \langle \psi_{\ell}^{(2)}(\vec{v}_2), ^{(2)}\Lambda_{\vec{k}}^{(2,1)} \psi_m^{(1)}(\vec{v}_1) \rangle_2 \\
 & \langle \langle \vec{\psi}_{\ell}^{(2)}(\vec{v}_1, \vec{v}_2), \Lambda_{\vec{k}} \vec{\psi}_m^{(2)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 = \\
 & = \langle \psi_{\ell}^{(2)}(\vec{v}_2), ^{(1)}\Lambda^{(2,2)} \psi_m^{(2)}(\vec{v}_2) \rangle_2 + \langle \psi_{\ell}^{(2)}(\vec{v}_2), ^{(2)}\Lambda_{\vec{k}}^{(2,2)} \psi_m^{(2)}(\vec{v}_2) \rangle_2
 \end{aligned}$$

Therefore, in principle, I have to compute the matrix elements of 6 operators: $^{(1)}\Lambda^{(1,1)}$, $^{(2)}\Lambda_{\vec{k}}^{(1,1)}$, $^{(2)}\Lambda_{\vec{k}}^{(1,2)}$, $^{(2)}\Lambda_{\vec{k}}^{(2,1)}$, $^{(1)}\Lambda^{(2,2)}$ and $^{(2)}\Lambda_{\vec{k}}^{(2,2)}$. But this number can be reduced. First of all, because of the

symmetry of $\bar{\Lambda}_{\vec{k}}$ (or $\Lambda_{\vec{k}}$ for $\ell, m \neq 1$), the (ℓ, m) element of $^{(2)}\Lambda_{\vec{k}}^{(1,2)}$ is equal to the (m, ℓ) element of $^{(2)}\Lambda_{\vec{k}}^{(2,1)}$. However, I will now show that I need the matrix elements of only two operators.

To do this, let me first consider the subdivision of $^{(1)}\Lambda^{(i,i)}$ into two parts, given by the two terms on the right-hand side of (2.87):

$$\begin{aligned}
 {}^{(1)}\Lambda^{(i,i)} f(\vec{v}_i) = & \sum_{i'=1}^2 n_{i'} \chi_{ii'} \sigma_{ii'}^2 \int d\sigma d\vec{v}_3 \hat{\phi}_0^{(i')}(\vec{v}_3) |\vec{v}_{i3}^{(i,i')} \cdot \hat{\sigma}| \times \\
 & \times \theta(\vec{v}_{i3}^{(i,i')} \cdot \hat{\sigma}) [b_{i3}^{(i,i')}(\sigma) - 1] f(\vec{v}_i)
 \end{aligned} \quad (3.3)$$

where one term has $i'=i$ and the other has $i' \neq i$. The first term ($i'=1$) describes collisions between like particles, the second term ($i' \neq i$) collisions between unlike particles. In the same way, ${}^{(2)}\Lambda_{\vec{k}}^{(i,i)}$ describes collisions between like particles, while ${}^{(2)}\Lambda_{\vec{k}}^{(i,j)}$, with $i \neq j$, accounts for collisions between unlike particles. From all this follows that it is sufficient to compute the matrix elements of the second term of ${}^{(1)}\Lambda^{(1,1)}$, which, in (3.3), is the term with $i'=2$, and of ${}^{(2)}\Lambda_{\vec{k}}^{(1,2)}$, both of which involve collisions between particles of species 1, with mass m_1 , and particles of species 2, with mass m_2 . Apart from overall factors (like $n_i \chi_{ii'} \sigma_{ii'}^2$, in (3.3)), the matrix elements of the other operators will follow easily. For the term of ${}^{(1)}\Lambda^{(1,1)}$ with $i'=1$ and for ${}^{(2)}\Lambda_{\vec{k}}^{(1,1)}$ we can obtain its matrix elements replacing the masses m_1, m_2 by the masses m_1, m_1 , since we have a general expression for any m_1, m_2 ; for the term of ${}^{(1)}\Lambda^{(2,2)}$ with $i'=2$ and for ${}^{(2)}\Lambda_{\vec{k}}^{(2,2)}$ one replaces the masses m_1, m_2 by m_2, m_2 ; for the term of ${}^{(1)}\Lambda^{(2,2)}$ with $i'=1$ one replaces m_1, m_2 by m_2, m_1 . The operator ${}^{(2)}\Lambda_{\vec{k}}^{(2,1)}$, as mentioned above, follows by symmetry from ${}^{(2)}\Lambda_{\vec{k}}^{(1,2)}$.

Next I will give some details on how the computation of the matrix elements is performed.

The first few matrix elements, involving the first few polynomials, could be computed by direct substitution of the expressions of the polynomials in the integrals. But this direct evaluation becomes very soon unreasonably long, with increasing the value of the indices (r,s) of the

polynomials $\psi_{r,s}(\vec{c})$. Thus it is more convenient to use a procedure involving generating functions, that gives the possibility to obtain a general expression that will depend on the indices r, s and r', s' of the two polynomials involved in the matrix element.

The functions $\psi_{r,s}(\vec{c})$ are polynomials in $c=|\vec{c}|$ and c_z , resulting from a product of a spherical harmonic $Y_s^{(0)}(c_z/c)$, proportional to the Legendre polynomial P_s of degree s , a Sonine polynomial $S_r^{(s+1/2)}(c^2)$, and c^s . As mentioned in Chapter II, the Sonine polynomials are related to the associated Laguerre polynomials through a multiplicative factor. General expressions are known both for the Legendre and Laguerre¹³⁾ polynomials, with coefficients given as a function of, respectively, the index s of the Legendre polynomial, and the two indices r and s of the Laguerre polynomial. Therefore it is possible to write down general expressions for the functions $\psi_{r,s}(\vec{c})$. This expressions is a sum of terms, each of which is proportional to a product of powers of c^2 and c_z respectively, i. e., each term is of the form:

$$(c^2)^p c_z^q \quad (3.4)$$

Therefore, if I compute the matrix elements involving terms of the form (3.4) for general values of p, q , I can derive the matrix elements involving the functions $\psi_{r,s}(\vec{c})$.

In the computation of the matrix elements between two terms of the form (3.4), I have employed generating functions. In fact (3.4) can also be written as:

$$\left(\frac{\partial}{\partial t_1}\right)_0^p \left(\frac{\partial}{\partial t_2}\right)_0^q e^{t_1 c^2 + t_2 c_z} \quad (3.5)$$

where the subscript zero in the derivatives means that after differentiation the corresponding variable is set equal to zero. Then, computing the matrix elements between the two functions:

$$e^{t_1 c^2 + t_2 c_z}; \quad e^{t_3 c^2 + t_4 c_z} \quad (3.6)$$

the matrix elements between two terms of the form (3.4), with p, q and p', q' respectively, will be obtained differentiating, with respect to t_1, t_2, t_3, t_4 , the matrix elements between the two functions (3.6), respectively p, q, p' and q' times, and putting successively $t_1=t_2=t_3=t_4=0$.

3.3 The matrix $A(k, z)$

I am left with the computation of the matrix elements (2.103):

$$A_{\ell m}^{(i, j)}(k, z) = \delta_{ij} \langle \psi_{\ell}^{(i)}(\vec{v}_1, \vec{v}_2) \frac{1}{z + i k v_{1z} - d(k)} \psi_m^{(j)}(\vec{v}_1, \vec{v}_2) \rangle_1 \rangle_2 \quad (3.7)$$

they vanish if $i \neq j$. For $i=j$ we have:

$$\begin{aligned} A_{\ell m}^{(1, 1)}(k, z) &= \langle \psi_{\ell}^{(1)}(\vec{v}_1) \frac{1}{z + i k v_{1z} - d(k)} \psi_m^{(1)}(\vec{v}_1) \rangle_1 \\ &= \left(\frac{\beta_{m1}}{2\pi} \right)^{3/2} \int d\vec{v}_1 e^{-\beta_{m1} v_1^2 / 2} \psi_{\ell}^{(1)}(\vec{v}_1) \frac{1}{z + i k v_{1z} - d(k)} \psi_m^{(1)}(\vec{v}_1) = \\ &= -i \left(\frac{\beta_{m1}}{2\pi} \right)^{1/2} \frac{1}{k} A_{\ell m}(\xi_1) \end{aligned} \quad (3.8)$$

with:

$$\begin{aligned} A_{\ell m}(\xi_1) &= \left(\frac{1}{\pi} \right)^{3/2} \int d\vec{c} e^{-c^2} \psi_{\ell}(\vec{c}) \frac{1}{c_z - \xi_1} \psi_m(\vec{c}); \\ \xi_1 &= i \left(\frac{\beta_{m1}}{2} \right)^{1/2} \frac{1}{k} (z - d(k)) \end{aligned} \quad (3.9)$$

In the same way:

$$\begin{aligned} A_{\ell m}^{(2, 2)}(k, z) &= -i \left(\frac{\beta_{m2}}{2\pi} \right)^{1/2} \frac{1}{k} A_{\ell m}(\xi_2) \\ \xi_2 &= i \left(\frac{\beta_{m2}}{2} \right)^{1/2} \frac{1}{k} (z - d(k)) \end{aligned} \quad (3.10)$$

The functions $A_{\ell m}(\xi)$ ($\xi=\xi_1, \xi_2$) are closely related to the plasma dispersion function $Z(\xi)$, which is defined, for $\text{Im } \xi > 0$, by:

$$Z(\xi) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} dx \frac{e^{-x^2}}{x-\xi} \quad (3.11)$$

For $\text{Im } \xi < 0$ the plasma dispersion function is the analytic continuation of (3.11). The function, so defined in the whole complex plane, is analytic everywhere with an essential singularity for $\text{Im } \xi \rightarrow -\infty$, of the form $e^{-\xi^2}$. Also the functions $A_{\ell m}(\xi)$ are to be understood as defined by (3.9) for $\text{Im } \xi > 0$ and by its analytic continuation for $\text{Im } \xi < 0$. Since $d(k)$ is always a (negative) real number, it follows from the definition of ξ (cf. (3.30) or (3.31)) that $A_{\ell m}^{(i,i)}(k,z)$ are defined by (3.9) (for $i=j$) if $\text{Re } z > d(k)$, and by its analytic continuation for $\text{Re } z \leq d(k)$. This interpretation has to be preferred above the other possible one in which $A_{\ell m}^{(i,i)}$ are defined by (3.9) for both the regions $\text{Re } z > d(k)$ and $\text{Re } z < d(k)$; in this case the two functions so defined (one for $\text{Re } z > d(k)$ and the other for $\text{Re } z < d(k)$) are not each other's analytic continuation, and they tend to different limits when $\text{Re } z \rightarrow d(k)$. Alternatively, we can speak, in this interpretation, of a single function $A_{\ell m}^{(i,i)}$ with a line of discontinuity for $\text{Re } z = d(k)$. The reason to choose the former interpretation rather than the latter is the following. The value of $d(k)$ has nothing special from the physical point of view; we could have chosen another value, and this would have changed, in the second interpretation, the line of discontinuity for $A_{\ell m}^{(i,j)}(k,z)$. Besides, it can be shown that in this case, for that value of k for which the real part of a solution (i. e. an eigenvalue) of the equation (2.104) ($D(k,z)=0$) reaches the value $d(k)$, then the solution of that equation for that particular eigenvalue can no longer be obtained. We would therefore find ourselves in a

situation in which the eigenvalues exist only in a limited range of k , that would in addition depend on the value of $d(k)$. I therefore adopt the interpretation that $A_{\ell m}^{(i,i)}(k,z)$ are defined by (3.7) for $\text{Re } z > d(k)$ and by its analytic continuation for $\text{Re } z \leq d(k)$.

In this case a general result has been derived for the $A_{\ell m}(\xi)$, which is the following¹¹⁾:

$$A_{\ell m}(\xi) = B_{\ell m}^{(1)}(\xi) + B_{\ell m}^{(2)}(\xi)Z(\xi) \quad (3.12)$$

where $B^{(1)}(\xi)$ and $B^{(2)}(\xi)$ are polynomials, that I do not reproduce here. This formula is exact for all values of ξ . From it we see that $A_{\ell m}^{(i,i)}(k,z)$, as anticipated in the previous chapter, has an essential singularity when $\text{Im } \xi \rightarrow -\infty$ (since $Z(\xi)$ has one), i. e., when $\text{Re } z \rightarrow -\infty$.

3.4 The static structure factors $S_{ij}(k)$

The computation of the static structure factors $S_{ij}(k)$ (or, equivalently, of the radial distribution functions $g_{ij}(r)$) can in general be performed only approximately. For the hard sphere potential, like for other short range potentials, a good approximation is the Percus-Yevick equation. I will say only the following about this equation, referring to the literature for details. The Percus-Yevick equation leads to explicit expressions for the partial direct correlation functions, to be defined shortly, and these, as will be explained below, allow to compute the static structure factors $S_{ij}(k)$.

The partial direct correlation functions $C_{ij}(r)$ are defined by the following equations:

$$g_{ij}(r) - 1 = C_{ij}(r) + \sum_{\ell=1}^2 n_{\ell} \int d\vec{r}' (g_{i\ell}(r') - 1) C_{\ell j}(|\vec{r} - \vec{r}'|); \quad i, j=1,2 \quad (3.13)$$

This definition may seem quite arbitrary; its meaning becomes clear, for example, in a systematic study of the radial distribution functions $g_{ij}(r)$ through the method of diagrammatic expansions, which is not of interest here, and for which I refer to the literature²⁾. The functions $g_{ij}(r)-1$ are usually denoted by $h_{ij}(r)$, and called pair correlation functions. To solve (3.13), one uses Fourier transforms. If $h_{ij}(k)$ and $C_{ij}(k)$ are the spatial Fourier transform of, respectively, $h_{ij}(r)$ and $C_{ij}(r)$, then the spatial Fourier transform of (3.13) gives:

$$h_{ij}(k) = C_{ij}(k) + \sum_{\ell=1}^2 n_{\ell} h_{i\ell}(k) C_{\ell j}(k) \quad (3.14)$$

Written in matrix form, this equation is:

$$h(k) = C(k) + h(k)C'(k) \quad (3.15)$$

where $h(k)$ ($C(k)$) is the 2×2 matrix with elements $h_{ij}(k)$ ($C_{ij}(k)$), and $C'(k)$ is the 2×2 matrix with elements $C'_{ij}(k) = n_i C_{ij}(k)$. On the other hand, if I denote with $S'(k)$ the matrix with elements $S'_{ij}(k)$, (1.18) shows that:

$$S'(k) = I + h'(k) \quad (3.16)$$

where I is the unit matrix, and $h'(k)$ the matrix with elements $h'_{ij}(k) = \sqrt{n_i n_j} h_{ij}(k)$. Therefore, knowing $C(k)$, and therefore $C'(k)$, one can find $h(k)$, and $h'(k)$, and then $S'(k)$. Explicitly, if p is the diagonal matrix with elements $p_{ij} = \delta_{ij} n_i$ and q the diagonal matrix with elements $q_{ij} = \delta_{ij} \sqrt{n_i}$, so that $C'(k) = p C(k)$ and $h'(k) = q h(k) q$, we have from (3.15):

$$h(k) = C(k) [I - p C(k)]^{-1} \quad (3.17)$$

Then, from (3.16) we find:

$$\begin{aligned} S'(k) &= I + q h(k) q = I + q C(k) [I - p C(k)]^{-1} q = \\ &= [q^{-1} [I - p C(k)] + q C(k)] [I - p C(k)]^{-1} q = q^{-1} [I - p C(k)]^{-1} q \end{aligned} \quad (3.18)$$

where in the last equality I have used the obvious relation $q^{-1}p=q$. This shows how, from the knowledge of $C_{ij}(k)$, one can compute the $S_{ij}(k)$.

3.5 The velocity of sound and the χ_{ij}

Although for consistency I should use the Percus-Yevick equation also for the velocity of sound and the χ_{ij} , better results are obtained using a phenomenological equation of state, given below. This equation, however, cannot be used to compute the $S_{ij}(k)$, since it does not provide the functions $g_{ij}(r)$, whose Fourier transforms are the $S_{ij}(k)$.

With the method of diagrammatic expansions, mentioned in the last section, one can derive different approximate equations of state. For hard spheres, however, computer simulations have shown that the most successful equation of state, up to high densities, is a heuristic equation of state proposed by Carnahan and Starling. For binary mixtures it gives the pressure p as a function of the temperature T and the number densities n_1 and n_2 by:

$$p = \frac{6k_B T}{\pi} \left[\frac{\eta_0}{(1-\eta_3)} + \frac{3\eta_1\eta_2}{(1-\eta_3)^2} + \frac{3\eta_2^3}{(1-\eta_3)^3} - \frac{\eta_3\eta_2^3}{(1-\eta_3)^3} \right] \quad (3.19)$$

where

$$\eta_\ell = \frac{\pi}{6} (n_1 \sigma_1^\ell + n_2 \sigma_2^\ell) \quad (3.20)$$

From (3.19) one can compute approximately the velocity of sound c_s , which is defined by:

$$c_s^2 = \gamma \left(\frac{\partial p}{\partial \rho} \right)_{T,c} \quad (3.21)$$

where $\rho = n_1 m_1 + n_2 m_2$ is the total mass density and $c = n_1 m_1 / \rho$ is the mass concentration of species 1; γ is the ratio of the specific heats at constant pressure and volume, respectively, for fixed mass concentration:

$$\gamma = \frac{C_{p,c}}{C_{v,c}} = \left(\frac{\partial S}{\partial T} \right)_{p,c} / \left(\frac{\partial S}{\partial T} \right)_{v,c} \quad (3.22)$$

Both γ and the derivatives on the right-hand side of (3.21) can be computed from (3.19). In fact, it follows from the theory of Jacobians that:

$$\left(\frac{\partial p}{\partial \rho} \right)_{T,c} = \frac{n_1}{n_1 m_1 + n_2 m_2} \left(\frac{\partial p}{\partial n_1} \right)_{n_2, T} + \frac{n_2}{n_1 m_1 + n_2 m_2} \left(\frac{\partial p}{\partial n_2} \right)_{n_1, T} \quad (3.23)$$

For γ I use the following thermodynamic relation between the specific heats per particle $c_{p,c} = C_{p,c}/N$ and $c_{v,c} = C_{v,c}/N$:

$$c_{p,c} = c_{v,c} + \frac{Tm}{\rho^2} \left(\frac{\partial p}{\partial T} \right)_{\rho,c}^2 / \left(\frac{\partial p}{\partial \rho} \right)_{T,c} \quad (3.24)$$

where $m = (n_1 m_1 + n_2 m_2) / (n_1 + n_2)$. The second term on the right-hand side can be computed from (3.19). For $c_{v,c}$ I use that for hard spheres the internal energy is purely kinetic, so that $c_{v,c} = 3k_B/2$.

Finally, I should note that also for the $\chi_{ij} = g_{ij}(\sigma_{ij})$, the radial distribution functions at contact, that appear in the collision operator, I have used the Carnahan-Starling approximation. The χ_{ij} are then given by:

$$\chi_{ij} = \frac{1}{1-\eta_3} + \frac{3\sigma_i \sigma_j}{\sigma_i + \sigma_j} \frac{\eta_2}{(1-\eta_3)^2} + 2 \left[\frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j} \right]^2 \frac{\eta_2}{(1-\eta_3)^2} \quad (3.25)$$

and are such that, if introduced into the exact relation:

$$p = k_B T \left[n_1 + n_2 + \frac{2}{3} \pi \sum_{i=1}^2 \sum_{j=1}^2 n_i n_j \sigma_{ij}^3 \chi_{ij} \right] \quad (3.26)$$

(that would give the exact equation of state if the χ_{ij} were exact), they give the Carnahan-Starling equation of state (3.19).

The results

It is natural to expect that binary mixtures offer a richer variety of features than simple fluids. The reason is that more parameters occur in the specification of the state of the system. In a simple fluid one has to know the temperature T and the density n [1] (or the reduced density $n^* = n\sigma^3$, which is proportional to the fraction of the total volume occupied by the spheres). In a binary mixture, besides the temperature, one has to specify the two partial densities n_1 and n_2 (or, equivalently, the total density $n = n_1 + n_2$ and the relative concentration of, say, the particles of species 1, x_1); in addition, one can still vary the ratio σ_1/σ_2 between the two diameters and the ratio m_1/m_2 between the two masses.

In this thesis the interest has been focused on properties of binary mixtures for which the masses of the two components are very different; they are called disparate-mass binary mixtures. The main point of the results can be summarized in the following.

In Chapter 2 I have introduced the discrete eigenvalues of the kinetic operator $L_E(\vec{k})$, and the corresponding amplitudes (cf. subsection 2.3.2). The eigenvalues can be divided into two types. One type is made of complex eigenvalues, and the other type of real eigenvalues. For both types the real part is always negative¹²⁾. The eigenvalues belonging to the first type come in complex conjugate pairs. The complex eigenvalues describe propagating, and damped, processes: the real part represents the damping, while the imaginary part represents the propagation; two complex conjugate eigenvalues

represent propagation in opposite directions. The real eigenvalues represent purely damped (diffusive) processes. As will be explained later, in all the cases studied in this thesis the computation of the density-density correlation functions using only the discrete eigenvalues gives results which are identical to those given by the "exact" computation, as given by the matrix inversion formula (2.102). Therefore the dynamical processes that determine the $S_{ij}(k, \omega)$ can be explained in terms of only the discrete eigenvalues and the corresponding amplitudes, that describe the different modes by which the correlations decay in time. What I found, in disparate-mass binary mixtures, is the appearance of a fast propagating mode, i. e., a mode associated with an eigenvalue with a large velocity of propagation. The main properties of this mode are the following. It is present in a vast range of densities, from dilute gas mixtures to rather high (liquid) densities. This mode appears beyond the hydrodynamic regime, namely for k values for which the hydrodynamic description is not good. Most important, the fast mode is associated with the dynamics of the light component only; in fact it gives a visible contribution only to $S_{11}(k, \omega)$ (if 1 is the light component), and not to $S_{12}(k, \omega)$ and $S_{22}(k, \omega)$. The fast mode can be called fast sound, because, like the ordinary sound, it propagates, but it is faster.

In section 4.1 I will say something about previous results on disparate-mass binary mixtures. In section 4.2 I will show the connection between the density of the mixture and the kind of experiments necessary to test the predictions on fast sound made in this thesis. In section 4.3 more details will be given on fast sound. In sections 4.4 through 4.6 the results

for dilute mixtures will be presented, while the sections 4.7 through 4.9 will treat dense mixtures.

4.1 Some previous results on disparate-mass binary mixtures

The fact that the particles of the two species have very different masses causes a characteristic behavior that was noticed already many years ago by Grad¹⁴⁾ for dilute gas mixtures. He pointed out that for such mixtures the exchange of kinetic energy between light and heavy molecules is very slow, so that the approach to equilibrium occurs in two stages. First each one of the two species reaches local equilibrium with its own temperature, and then equilibration of the two different temperatures takes place. As a consequence, Grad's suggestion was to use, as a first step beyond hydrodynamics, a set of hydrodynamic equations in which one additional variable would be present; namely instead of one temperature for the whole mixture, one should distinguish two temperatures: one associated with the light component and one associated with the heavy component (two-temperature hydrodynamics). This idea was further developed by others, especially by Johnson and co-workers¹⁵⁾ and by Kamgar-Parsi and Cohen¹⁶⁾, who studied the behavior of forced sound modes, as a function of the frequency ω of an external disturbance [2] in dilute binary mixtures of He and Xe. For He concentrations $x_1 > 0.45$ and frequencies $\omega > 10^8$ Hz, a sharp increase in the forced sound velocity was found.

A computer simulation on a liquid alloy¹⁷⁾, which has a bearing on the results of this thesis, will be mentioned in somewhat greater detail later in the chapter.

4.2 Neutron scattering and light scattering in disparate-mass mixtures

From the previous studies of disparate-mass binary mixtures it is clear that characteristic phenomena would occur outside the hydrodynamic regime; for sufficiently small k and ω the mixture behaves according to the usual hydrodynamics equations for mixtures. For an experimental study of the range of validity of the hydrodynamic equations in dilute He-Xe mixtures see, for example, Letamendia et al.¹⁸⁾

I gave already some indications, in subsection 1.1.5, of the range of k and ω values for which one expects hydrodynamics to hold. The purpose of this section is to give more quantitative arguments, so that I will then be able to explain the relation between the density of the disparate-mass binary mixture, and the kind of experiment (i. e., the choice between light scattering and neutron scattering) one has to perform in order to test the predictions presented later in this thesis.

4.2.1 Mean free path and mean free time

I said that in hydrodynamics k and ω must be small in the sense that k has to be small compared to the inverse of any typical microscopic length, and ω has to be small compared to the inverse of any microscopic relaxation time. As a typical microscopic length one can take the mean free path of a particle, i. e. the average distance travelled by a particle between two successive collisions. However, while in simple fluids this is a unique quantity, in a binary mixture the average distance between two successive collisions will be different for particles of different species. I will give

now explicit expressions. In a simple fluid of hard spheres of diameter σ one can show that the mean free path is given by:

$$\ell = \frac{1}{\sqrt{2}\pi n \sigma^2 \chi} \quad (4.1)$$

where I recall that χ is the radial distribution function at contact: $\chi = g(\sigma)$. We see that ℓ is inversely proportional to the factor $n\sigma^2\chi$ and that it does not depend on the temperature ($g(r)$ for hard spheres depends only on the density and not on the temperature). Since, when $n \rightarrow 0$, then $\chi \rightarrow 1$, in first approximation in the density ℓ is inversely proportional to $n\sigma^2$, which could have been guessed on dimensional grounds.

In a binary mixture one has two mean free paths, one, ℓ_1 , for particles of species 1, and one, ℓ_2 , for particles of species 2. They are given by the following generalizations of (4.1):

$$\frac{1}{\ell_1} = \sqrt{2}\pi n_1 \sigma_1^2 \chi_{11} + \left(1 + \frac{m_1}{m_2}\right)^{1/2} \pi n_2 \sigma_{12}^2 \chi_{12} \quad (4.2)$$

$$\frac{1}{\ell_2} = \sqrt{2}\pi n_2 \sigma_2^2 \chi_{22} + \left(1 + \frac{m_2}{m_1}\right)^{1/2} \pi n_1 \sigma_{12}^2 \chi_{12} \quad (4.3)$$

Like ℓ in a simple fluid, also ℓ_1 and ℓ_2 do not depend on the temperature, but only on the partial densities n_1 and n_2 (χ_{ij} 's depend only on n_1, n_2). The results (4.2) and (4.3) are simple generalizations, to high densities, of the mean free paths in dilute hard sphere mixtures, which can be found in the first of Ref. 3; the only difference is the presence of the χ_{ij} . The first term in (4.2) is the inverse of the average distance travelled by a particle of species 1 between two successive collisions with particles of species 1, while the second term is the inverse of the average distance travelled by a particle of species 1 between two collisions with particles of species 2. These two distances can be denoted, respectively, by $\ell_{1,1}$ and $\ell_{1,2}$, so that we have:

$$\frac{1}{\ell_1} = \frac{1}{\ell_{1,1}} + \frac{1}{\ell_{1,2}} \quad (4.4)$$

That ℓ_1 is given in terms of $\ell_{1,1}$ and $\ell_{1,2}$ by (4.4) can be understood in the following way. If a particle of species 1 travels a distance L , then it experiences $L/\ell_{1,1}$ collisions with like particles and $L/\ell_{1,2}$ collisions with particles of species 2; therefore the average distance ℓ_1 between any two collisions is given by L divided by the total number of collisions:

$$\ell_1 = \frac{L}{\frac{L}{\ell_{1,1}} + \frac{L}{\ell_{1,2}}} \quad (4.5)$$

which is exactly (4.4). The same kind of analysis holds for ℓ_2 ; we write:

$$\frac{1}{\ell_2} = \frac{1}{\ell_{2,2}} + \frac{1}{\ell_{2,1}} \quad (4.6)$$

where the two terms on the right-hand side correspond to the two terms on the right-hand side of (4.3). The first term involves $\ell_{2,2}$, the average distance travelled by a particle of species 2 between two successive collisions with particles of species 2, and the second term involves $\ell_{2,1}$, the average distance travelled by a particle of species 2 between two successive collisions with particles of species 1.

With these definitions I can give a more precise meaning to the smallness of the wavevector k . One can say that k is small when the products $k\ell_1$ and $k\ell_2$ are both small numbers compared to 1. This means that the wavelength λ associated with k , $\lambda=2\pi/k$, is large compared to ℓ_1 and ℓ_2 [3]. This assures that inside one wavelength many collisions can take place, a necessary condition for local equilibrium and the validity of the hydrodynamic description. The other condition is that one has to consider times large enough that these collisions have actually taken place. This will be satisfied if we study frequencies ω such that ωt_E is small compared to 1, where t_E is a convenient average time between collisions (mean free

time). I use the subscript E because, as will be explained in a moment, τ_E is derived from the kinetic operator $L_E(\vec{k})$. An average time between collisions is provided, in our kinetic theory, by the collision operator; in fact the matrix elements of the collision operator are proportional to the average frequency of the collisions, or to the inverse time between collisions. The calculation of the matrix elements of the collision operator shows that a convenient definition for τ_E is:

$$\tau_E = \frac{\sqrt{2\beta\mu}}{4\sqrt{\pi n\sigma_{12}^2\chi_{12}}} \quad (4.7)$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass. The factors are chosen in such a way that τ_E reduces to the simple fluid mean free time when the two components are identical.

4.2.2 Rarefied and dense mixtures

The change of the value of ℓ_1 and ℓ_2 with the density is at the basis of the kind of experiment one has to perform to test the predictions presented in this thesis. Throughout this chapter I will use the reduced (dimensionless) density n^* defined by $n^* = n_1 \sigma_1^3 + n_2 \sigma_2^3$. I want to show that for dilute mixtures the appropriate experiments are those of light scattering, while for dense mixtures experiments of neutron scattering are necessary.

In a dilute mixture n^* is a small number compared to 1: the volume occupied by the particles is very small compared to the total volume. When $n^* \ll 1$ the mixture is very close to a mixture of ideal gases; in fact in this case all the approximate equations of state, in particular also (3.19), approach the ideal gas equation of state, $p = nk_B T$, with $n = n_1 + n_2$. To give an

example, a fluid (simple or binary mixture) at a pressure of 1 atmosphere at room temperature is practically an ideal gas, and has n^* of the order of magnitude of 10^{-3} . If one computes the mean free paths ℓ_1 and ℓ_2 for such values of n^* , one finds that they have an order of magnitude of 10^{-5} cm. I will be primarily concerned, both for dilute and for dense mixtures, with phenomena occurring at a wavelength comparable to the mean free path. Therefore we see that for dilute mixtures we need to have probing wavelengths of the order 10^{-5} cm, which is in the range of visible electromagnetic radiation. So light scattering experiments will be appropriate in the study of such mixtures.

On the other hand, for densities in the range of dense gases or liquids, where n^* is of order 1, the mean free paths are of order 10^{-8} cm, which is in the range of wavelengths of thermal neutrons. Therefore for dense fluids the appropriate experiments are those of neutron scattering.

4.3 Fast sound propagation: an introduction

In this section I introduce the main subject of the results in this thesis, namely the fast sound propagation in disparate-mass binary mixtures.

4.3.1 Hydrodynamic limit

One can represent the density-density correlation functions $F_{ij}(k, t)$ with the discrete eigenvalues of $L_E(\vec{k})$, as mentioned in subsection 2.3.2, where the BGK method is explained. Then one has:

$$F_{ij}(k, t) = \sum_n A_{ij,n}(k) e^{z_n(k)t} \quad (4.8)$$

where, with $A_{ij,n}$, I have indicated the amplitude corresponding to the eigenvalue $z_n(k)$. The number of terms in the sum depends on the approximation employed, i. e., on the number of polynomials used (in the approximation of order M , $2M$ polynomials are used), and the $A_{ij,n}(k)$ are related to the $M_{11,n}^{(i,j)}$ of subsection 2.3.2 (I recall that $F_{ij}(k,t)=F_{11}^{(i,j)}(k,t)$); the relation is obtained with the use of (2.93). For $k \rightarrow 0$ we recover the results of hydrodynamics, in the following sense. With the use of the hydrodynamic equations one gets expressions for the F_{ij} 's like (4.8), with the sum running from 1 to 4. Two eigenvalues are each other's complex conjugates and correspond to sound propagation in the two opposite directions parallel to \vec{k} :

$$z_{1,2}^{(h)}(k) = \pm i c_s k - \Gamma k^2 \quad (4.9)$$

where the superscript (h) means that this is a result from hydrodynamics; c_s is the adiabatic velocity of sound and Γ is the sound damping coefficient. The other two eigenvalues are real and correspond to purely diffusive (non propagating) behavior:

$$z_3^{(h)}(k) = -D_1 k^2; \quad z_4^{(h)}(k) = -D_2 k^2 \quad (4.10)$$

The coefficients Γ , D_1 and D_2 are combinations of the thermodynamic quantities and transport coefficients of the mixture, which are not of interest here. For a description of the hydrodynamics equations in mixtures see, for example, Ref. 19. The point is that, when kl_1 and kl_2 are much smaller than 1, four of the eigenvalues of $L_E(\vec{k})$ in the sum (4.8) reduce to the values (4.9) and (4.10) (with explicit expressions for the transport coefficients that occur in Γ , D_1 and D_2 in terms of the diameters and masses of the two components), and also the corresponding amplitudes reduce to the hydrodynamic values $A_{ij,n}^{(h)}$ ($n=1,2,3,4$). The contributions of the other

eigenvalues of $L_E(\vec{k})$ to the sum is then negligible, since they are all real (for $k \rightarrow 0$) with an absolute value much larger than Γk^2 , $D_1 k^2$, $D_2 k^2$, and in addition the corresponding amplitudes are much smaller than the amplitudes corresponding to the first four modes. In this sense hydrodynamics is recovered in kinetic theory. Following the above correspondence, those 4 eigenvalues, in kinetic theory, that for small k reduce to the hydrodynamic result, are called extended hydrodynamic eigenvalues. The word "extended" means that, in kinetic theory, these eigenvalues acquire a meaning for k values beyond the hydrodynamic region. The other eigenvalues are called kinetic eigenvalues. I add here a remark on the terminology that I will employ in the following. For each n in (4.8), the corresponding eigenvalue z_n and the amplitudes A_{ij} are indicated collectively as an eigenmode. As anticipated in section 4.1, for each complex eigenvalue there is also the complex conjugate eigenvalue: these eigenvalues correspond to propagating (in opposite directions) eigenmodes; to real eigenvalues correspond non propagating eigenmodes. However, in the following, with propagating eigenmode, or, for brevity, mode, I will mean both eigenmodes, that propagate in opposite directions, together. Corresponding to the distinction between (extended) hydrodynamic eigenvalues and kinetic eigenvalues, also the eigenmodes can be separated in (extended) hydrodynamic eigenmodes and kinetic eigenmodes. As mentioned above, for a region in k around $k=0$, the only propagating eigenmodes are the hydrodynamic ones. In that region all the eigenvalues corresponding to the kinetic eigenmodes are real, and besides, contrary to the eigenvalues corresponding to the hydrodynamic eigenmodes, these real parts tend to a finite ($\neq 0$) limit when $k \rightarrow 0$.

4.3.2 Larger values of k, beyond hydrodynamics

In scattering experiments the relevant quantities are the $S_{ij}(k, \omega)$, that, with the $F_{ij}(k, t)$ given by (4.8), are obtained from the expressions:

$$S_{ij}(k, \omega) = \frac{1}{\pi} \sum_n \operatorname{Re} \frac{A_{ij,n}(k)}{i\omega - z_n(k)} \quad (4.11)$$

In the hydrodynamic limit we have:

$$S_{ij}^{(h)}(k, \omega) = \frac{1}{\pi} \sum_{n=1}^4 A_{ij,n}^{(h)} \operatorname{Re} \frac{1}{i\omega - z_n(k)} \quad (4.12)$$

where the amplitudes $A_{ij,n}^{(h)}$ are real. Introducing the values (4.9) and (4.10) we find:

$$S_{ij}^{(h)}(k, \omega) = \frac{1}{\pi} \left[\frac{A_{ij,1}^{(h)} \Gamma k^2}{(\omega - c_s k)^2 + (\Gamma k^2)^2} + \frac{A_{ij,2}^{(h)} \Gamma k^2}{(\omega + c_s k)^2 + (\Gamma k^2)^2} + \frac{A_{ij,3}^{(h)} D_1 k^2}{\omega^2 + (D_1 k^2)^2} + \frac{A_{ij,4}^{(h)} D_2 k^2}{\omega^2 + (D_2 k^2)^2} \right] \quad (4.13)$$

Each term in (4.13) is, for fixed k, a Lorentzian as a function of ω . Since $A_{ij,1}^{(h)}(k) = A_{ij,2}^{(h)}(k)$, $S_{ij}^{(h)}(k, \omega)$ is symmetric in ω , as it must be in a classical theory. The position of the center (i. e. the position of the peak) and the width and height of each Lorentzian is determined by the corresponding eigenvalue. So in (4.13) we have a Lorentzian centered at $\omega = c_s k$, another centered at $\omega = -c_s k$, both with width $2\Gamma k^2$; and two Lorentzians centered at $\omega = 0$. In Fig. (4.1) I show a typical shape of (4.13).

When we go beyond the hydrodynamic regime we can use the kinetic theory expression (4.11), when we use only the discrete eigenmodes of $L_E(\vec{k})$. Now in general the amplitudes $A_{ij,n}(k)$ of two propagating modes are complex, and the corresponding curves are not as simple as the ones in the first two terms in (4.13). More explicit expressions for the kind of functions

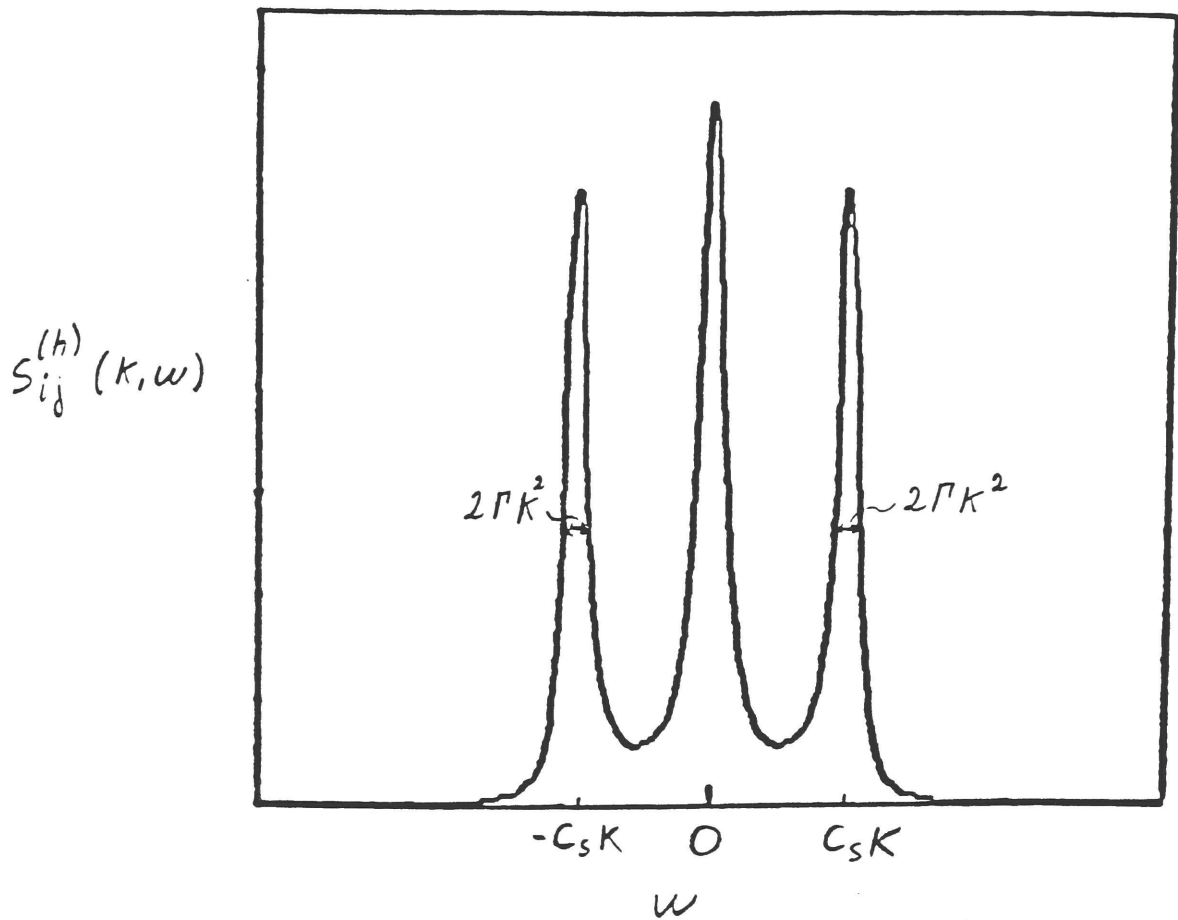


Fig. 4.1. A typical shape of the curve in (4.13). The widths of the side peaks are indicated. The central peak is given by the superposition of two Lorentzians.

obtained in this case (still called Lorentzians) will be given in the next section. The important point here is that generally we do not obtain a curve like that in Fig (4.1), with simply more peaks corresponding to the different propagating modes. The reason is the following. We write a general eigenvalue as $z_n(k) = i\omega_n(k) - \gamma_n(k)$, with $\gamma_n(k) > 0$. The function $\omega_n(k)$, the dispersion relation for the n -th mode, determines the velocity of propagation of the mode associated with $z_n(k)$. In fact the group velocity is given by $d\omega_n(k)/dk$. For the hydrodynamic sound mode (4.9) the group velocity is independent of k and is simply equal to the velocity of sound c_s . The value of $\gamma_n(k)$, as we have seen, determines the width and the height of the corresponding Lorentzian, when the amplitude is real. When the amplitude is complex the relation between $\gamma_n(k)$ and the shape of the Lorentzian is more complicated, but still $\gamma_n(k)$ is a measure of the range, around $\omega_n(k)$, over which the Lorentzian is significantly different from zero. Contrary to the hydrodynamic limit, where the ratio, for the relevant eigenvalues ($n=1,2,3,4$), of $\gamma_n(k)$ over $\omega_n(k)$ is small (cf. (4.9), which shows that this ratio goes to zero with k), outside the hydrodynamic regime in general $\gamma_n(k)$ and $\omega_n(k)$ are of the same order of magnitude. Therefore all the Lorentzians mix together in a complicated manner, so that no side peaks are visible, and a featureless bell shaped curve results.

In the results that I will present below, something new and different happens for disparate-mass binary mixtures. The details will be explained later; now I will give some general features.

Under certain conditions and for certain values of k , one of the eigenvalues $z_n(k)$ has an imaginary part $\omega_n(k)$ and a velocity of propagation $d\omega_n(k)/dk$ considerably larger than that of the other modes. This has the

following consequences. If the corresponding amplitude is not negligible, then the contribution of this mode to $S_{ij}(k, \omega)$ can be recognized, if not as a peak, then at least as an extended shoulder. There is then a visible contribution of this fast mode, but only to $S_{11}(k, \omega)$ (where with 1, I indicate the light component, and with 2 the heavy component). This implies that the fast mode is an important part of the dynamics, but only for the light component. If it is detected in actual scattering experiments on disparate-mass binary mixtures it would be the first time that a non hydrodynamic eigenmode in a fluid is clearly "seen". This is further discussed in the next sections.

4.4 Dilute mixtures: light scattering and polarizabilities

This and the next two sections will treat dilute mixtures. It is in dilute fluids where the hard sphere approximation is expected to work best. The reason is the following. In a dilute fluid with a realistic smooth (short range) potential it is very unlikely that more than two particles are, at the same time, in their mutual range of interaction, and, besides, the duration of a collision is much smaller than the time between two successive collisions. Therefore the real situation is close to that of a hard sphere fluid, where there are only binary collisions and the collisions are instantaneous, so that the ratio between the duration of a collision and the time between two successive collisions (the mean free time) is zero.

Another characteristic of the hard sphere potential is that it is spherically symmetric, so that it would seem that it cannot be used for molecules that do not possess spherical symmetry. However, again, in dilute

mixtures one expects that even if the molecules do not have spherical symmetry, the approximation introduced by the hard sphere potential does not do a real harm. As a matter of fact, the bulk of the results which I will present for dilute mixtures concern the study of H_2 -Ar mixtures: although the molecule of H_2 is not spherically symmetric, the reason to choose H_2 , rather than He, say, is the following. I want to study a binary mixture where the two components have very different masses. Among the noble gases this could be a He-Xe mixture, with a mass ratio m_2/m_1 of about 33, a He-Kr mixture, with a mass ratio of about 21, or a He-Ar mixture, with a mass ratio of about 10. But then one has to consider the problem raised by the value of the polarizabilities. We see from the expression (1.21), which gives the differential scattering cross section for light scattering, that, if, for example, $\alpha_1 \ll \alpha_2$, then practically only $S_{22}(k, \omega)$ is observed. This is contrary to what we want, since, as I have anticipated in the previous section, we would like to observe the contribution of $S_{11}(k, \omega)$, in which the fast mode manifests itself. In the He-Xe, He-Kr and He-Ar mixtures the contribution of $S_{11}(k, \omega)$ will hardly be seen (it is practically negligible for He-Xe), because the polarizabilities are very different. In fact $\alpha_{Ar} \approx 7.9\alpha_{He}$, $\alpha_{Kr} \approx 12.2\alpha_{He}$ and $\alpha_{Xe} \approx 19.6\alpha_{He}$. However, in a H_2 -Ar mixture the mass ratio is large, about 20, very similar to He-Kr, but the polarizability of Ar is only about twice as much as that of H_2 . This is because H_2 has a rather high polarizability for its mass.

I should add the following remark, on how the "equivalent" hard sphere diameter is chosen for a real gas of atoms or molecules. As mentioned in subsection 1.2.1 one can compute, with the help of the Enskog kinetic equation, the transport coefficients for hard spheres. Their value will

depend on the hard sphere diameter. The equivalent hard sphere diameter of a given atom or molecule is then chosen in such a way that the experimental value of a transport coefficient of the gas made of those atoms or molecules (usually the viscosity of that gas) agrees with that obtained on the basis of the Enskog theory. The values so obtained are then also used in the mixtures. The values for H_2 and Ar are, respectively, 2.760 Å and 3.659 Å, so that $\sigma_{12}=3.209$ Å. Their masses, in atomic units, are, respectively, 2.002 and 39.944.

In the next section I show the results for H_2 -Ar mixtures. In the section after the next I will give some results on other mixtures.

4.5 H_2 -Ar mixtures

In dilute mixtures, as mentioned in paragraph 4.2.2, the reduced density n^* has an order of magnitude of 10^{-3} . We can therefore roughly say that we consider reduced densities not higher than 10^{-2} . In this range of densities the mean free paths ℓ_1 , ℓ_2 are of the same order of the wavelength of visible light. Therefore with light scattering we probe wavevectors k for which $k\ell_1$, $k\ell_2$ are of order 1 and $k\sigma_1$, $k\sigma_2 \ll 1$. When this last condition is met, the k dependence of the collision operator can be neglected (cf. previous chapter). Besides, for dilute mixtures, the matrix elements of the mean field operator can be shown to be proportional to n^* , and therefore can also be neglected. The kinetic operator, where the k dependence of the collision operator is neglected, and also the mean field operator is neglected, is the Boltzmann operator. However, the calculations were performed exactly, without neglecting the k dependence of the collision

operator or the mean field operator, because that would not have implied a simplification in the computation. The argument is only given to show that for light scattering in dilute mixtures the only relevant lengths are ℓ_1 and ℓ_2 . For low densities the radial distribution functions at contact, χ_{ij} , are negligibly different from 1. Therefore, if we look at the mean free paths ℓ_1 and ℓ_2 given by (4.2) and (4.3), we see that for given relative concentrations of the two components, both ℓ_1 and ℓ_2 are inversely proportional to the density, in this range of low densities. So we expect that the results, always for fixed relative concentrations, will simply scale with the density. More precisely, if, for example, we find a certain function of k , $z_n(k)$, for one of the eigenvalues, then, if we increase the density by a factor a , we expect to find, for that eigenvalue, the function $z_n(ak)$. This is because increasing the density by a factor a , ℓ_1 and ℓ_2 are decreased by the same factor; therefore to have the same values of $k\ell_1$ and $k\ell_2$, which are the relevant parameters, we have to increase k by the same factor.

This is exactly what I found. Therefore in the following I will consider only one reduced density in H_2 -Ar mixtures, $n^*=0.005$, while I will vary the relative concentrations.

In the next subsection I will treat in many details the case where the relative concentration x_{H_2} of H_2 is 0.8. The second subsection of this section will concern other relative concentrations. In the last subsection I will draw some conclusions.

4.5.1 Relative concentration $x_{H_2}=0.8$

This is a rather long subsection. For more clarity I have divided it in two parts using roman numbers. In the first part I will give results concerning the most interesting range of k , using the BGK approximation with $2M=10$. In the second part I will show what happens if we improve the approximation, taking $2M=20$.

I $2M=10$ approximation

In Fig. (4.2) I show 8 eigenvalues, obtained in the BGK approximation with $2M=10$. They are the eigenvalues with the lowest real parts, in absolute value. In the following I explain how this and the following figures concerning the eigenvalues have to be interpreted. On the horizontal axis k is given in the dimensionless combination $k\sigma_{12}$; on the vertical axis the real parts of the eigenvalues are plotted on the negative side of the axis, while the absolute values of the imaginary parts are plotted on the positive side. These are made dimensionless multiplying by the mean free time t_E . Since complex eigenvalues come in complex conjugate pairs, each curve in the positive part of the vertical axis actually represents two eigenvalues, and so does the corresponding real part. At the value of k where two complex conjugate propagating eigenvalues appear, two real (non propagating) eigenvalues become equal.

We see in Fig. (4.2) that, for a value of $k\sigma_{12}$ roughly equal to 0.005, that corresponds to $k\ell_1=0.245$ and $k\ell_2=0.063$, a kinetic propagating mode begins to propagate at a velocity considerably faster than that of the

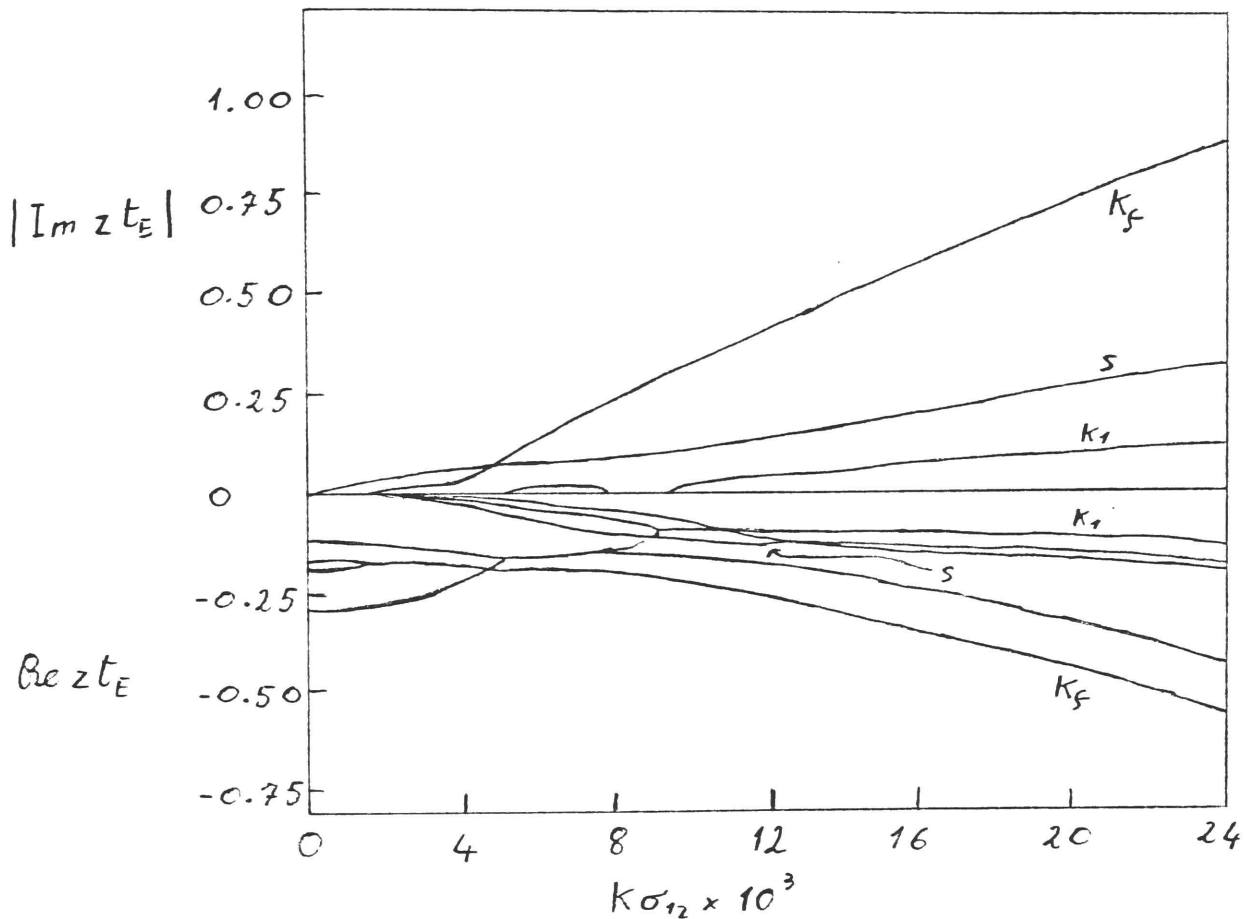
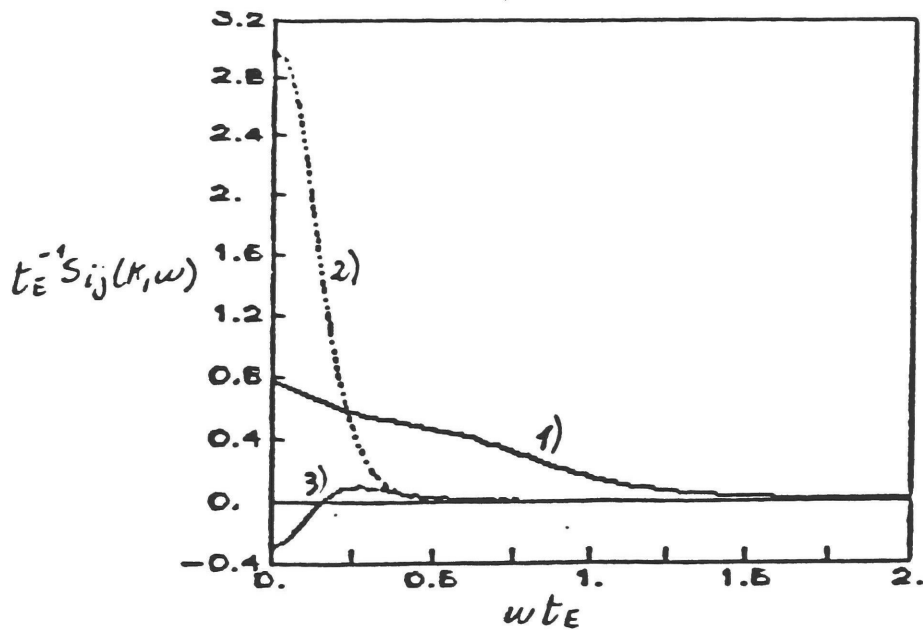
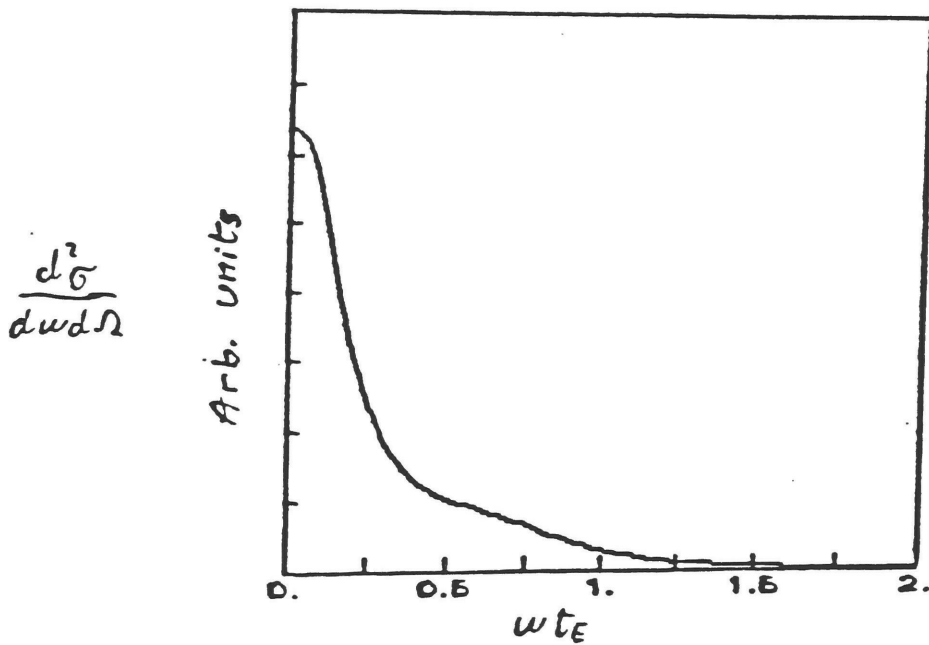


Fig. 4-2. 8 eigenvalues, obtained in the BGK approximation with $2M=10$, for H_2 -Ar with $n^*=0.005$ and $x_{H_2}=0.8$. K_F indicates the real and imaginary parts of the eigenvalue associated with the fast modes; S indicates the (extended) sound mode; K_1 indicates the other (slow) propagating mode. The eigenvalues associated with non propagating modes, and which have only a real part, are not marked with any character. As noted in the text, each curve in the positive part of the vertical axis actually represents the eigenvalues associated with two propagating modes (in opposite directions), and so does the corresponding real part; however, with propagating eigenmode, \pm indicates both eigenmodes, associated with the two eigenvalues.

(extended) sound. This kinetic mode begins to propagate at a value of k about $k\sigma_{12}=0.0025$, and in a short range of k changes its slope markedly (at about the same range in k a new kinetic propagating mode appears). Its damping, for the values of k for which it propagates fast, is larger than that of the other modes. In Fig. (4.2) the eigenvalue corresponding to this fast propagating mode is indicated with k_f . In order to see to what extent this fast mode is important in the density-density correlation functions, I have computed the $S_{ij}(k,\omega)$ for a value of $k\sigma_{12}=0.02$, where the fast mode has an imaginary part much larger than that of the other modes. Here I have used matrix inversion, as given by (2.102). In Fig. (4.3) I show the $S_{ij}(k,\omega)$ and the differential scattering cross section $d^2\sigma/d\omega d\Omega$. Here and in the following, I show only positive frequencies ω , since each $S_{ij}(k,\omega)$ is symmetric in ω . In Fig. (4.3), and in all the following figures showing the $S_{ij}(k,\omega)$, the frequency ω is made dimensionless by multiplication with the mean free time t_E (cf. (4.7)), while the $S_{ij}(k,\omega)$ are made dimensionless by dividing by t_E . Since for the differential scattering cross section I neglect multiplicative factors (cf. (1.21)), in the corresponding graphs I put arbitrary units. We see from Fig. (4.3) that the range, in ω , of $S_{11}(k,\omega)$, extends, with a pronounced shoulder, well beyond that of $S_{22}(k,\omega)$ and $S_{12}(k,\omega)$; the range of this shoulder is the same as that in which the fast mode occurs. This already gives a strong indication that the fast mode contributes only to $S_{11}(k,\omega)$. The shoulder in $S_{11}(k,\omega)$ is directly related to a shoulder in $d^2\sigma/d\omega d\Omega$, although this shoulder is much less pronounced. To verify directly the contribution of the fast mode, I have computed again the $S_{ij}(k,\omega)$ using only the discrete eigenvalues, like in (4.11). It turns out that using only the 8 eigenvalues, plotted in Fig. (4.2), the $S_{ij}(k,\omega)$



a)



b)

Fig. 4.3. a) $S_{ij}(k, \omega)$ for H_2 -Ar with $n^* = 0.005$ and $x_{H_2} = 0.8$. The value of $K\sigma_{12}$ is 0.02 : 1) $S_{11}(k, \omega)$; 2) $S_{22}(k, \omega)$; 3) $S_{12}(k, \omega)$. b) The differential scattering cross section.

obtained, are indistinguishable from those of Fig. (4.3). Therefore the contributions of the other two discrete eigenvalues, and of the essential singularity (cf. subsection 2.3.2) are negligible. Second, if we leave out the fast mode, then we obtain $S_{ij}(k, \omega)$ using only 6 discrete eigenvalues. The important point is that also in this case $S_{12}(k, \omega)$ and $S_{22}(k, \omega)$ are indistinguishable from those of Fig. (4.3); however $S_{11}(k, \omega)$ and, consequently, $d^2\sigma/d\omega d\Omega$, change appreciably. In Fig. (4.4) I show $S_{11}(k, \omega)$ and $d^2\sigma/d\omega d\Omega$ in the two different cases, matrix inversion like in Fig. (4.3), and with 6 discrete eigenvalues. This is a direct demonstration that the fast mode contributes only to $S_{11}(k, \omega)$, namely only to the dynamics of the light component. To give a more quantitative feeling of this I show, in Table (4.1), the amplitudes, corresponding to the 8 eigenvalues of Fig. (4.2), in the calculation of the $S_{ij}(k, \omega)$ with only these 6 discrete eigenvalues.

By comparing Fig. (4.2) and Table (4.1) I can make the following remarks.

a) Looking, in Table (4.1), at the amplitudes of the different modes that contribute to $S_{11}(k, \omega)$ and $S_{22}(k, \omega)$, we see that the main contribution comes from two separate sets of modes. Among the propagating modes, the largest contribution to $S_{11}(k, \omega)$ comes from the fast mode, while the largest contribution to $S_{22}(k, \omega)$ comes from the slowest of the three propagating modes. On the contrary $S_{12}(k, \omega)$ has amplitudes not extremely dissimilar among the different modes, although, as I mentioned above, neglect of the fast mode does not change $S_{12}(k, \omega)$ appreciably. Considering the non propagating modes, the main contribution to $S_{11}(k, \omega)$ and $S_{22}(k, \omega)$ comes,

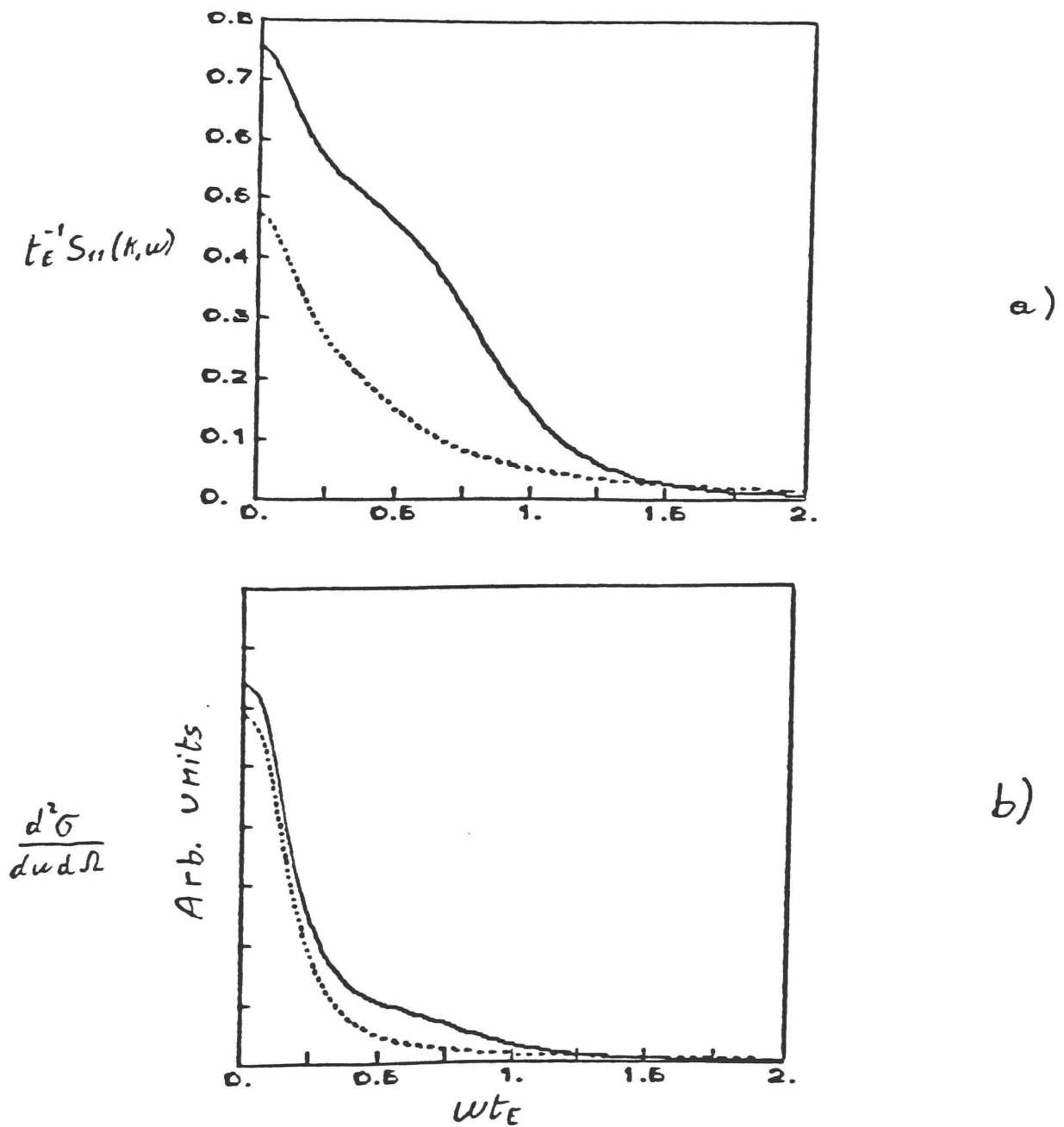


Fig. 4.4. a) $S_{11}(k, \omega)$ and b) $\frac{d^2\sigma}{d\omega d\Omega}$ for H_2 -Ar with $n^* = 0.005$ and $X_{H_2} = 0.8$. Full lines: matrix inversion, like in Fig. (4.3); dotted lines: using only 6 eigenvalues. The value of $k\sigma_n$ is 0.02, like in Fig. (4.3). For $S_{11}(k, \omega)$ the scale is different from that in Fig. (4.3). $S_{22}(k, \omega)$ and $S_{12}(k, \omega)$, computed using only 6 discrete eigenvalues, without the fast mode, are indistinguishable from those obtained version (see Fig. (4.2))

TABLE 4.1.

Amplitudes A_{ij} for the $S_{ij}(k, \omega)$, corresponding to the 8 eigenvalues of Fig. (4.2), for $k\omega = 0.02$. Here the eigenvalues associated with propagating modes are indicated with the same characters as in Fig. (4.2)

Eigenvalue	A_{11}	A_{22}	A_{12}
$-0.124 + 0.094i$ k_1	$-0.008 - 0.006i$	$0.464 - 0.431i$	$0.004 + 0.082i$
$-0.124 - 0.094i$ k_1	$-0.008 + 0.006i$	$0.464 + 0.431i$	$0.004 - 0.082i$
$-0.158 + 0.263i$ s	$-0.011 + 0.018i$	$-0.051 - 0.035i$	$0.048 + 7 \times 10^{-4}i$
$-0.158 - 0.263i$ s	$-0.011 - 0.018i$	$-0.051 + 0.035i$	$0.048 - 7 \times 10^{-4}i$
-0.176	0.034	0.175	-0.077
-0.338	0.500	5×10^{-5}	-0.005
$-0.450 + 0.724i$ k_f	$0.254 - 0.234i$	$-6 \times 10^{-5} + 3 \times 10^{-4}i$	$-0.011 - 0.005i$
$-0.450 - 0.724i$ k_f	$0.254 + 0.234i$	$-6 \times 10^{-5} - 3 \times 10^{-4}i$	$-0.011 + 0.005i$

respectively, from two different modes. The non propagating mode that contributes to $S_{22}(k, \omega)$ is also the one that contributes to $S_{12}(k, \omega)$.

b) One could then argue that, in this range of k where the fast mode occurs, the dynamics of the two components are quite separated. The most natural explanation for the negligible contribution of the fast propagating mode to the dynamics of the heavy component is that the heavy particles are unable to follow the rapid oscillations associated with the fast mode. Why the largest contribution, among the propagating modes, to $S_{11}(k, \omega)$ comes from the fast mode, rather than that the contributions from the various propagating modes are comparable, is not clear. I have to stress here that it is not a necessary condition, for the observability of the contribution of the fast mode to $S_{11}(k, \omega)$, that the largest contribution to $S_{11}(k, \omega)$, among the propagating modes, comes from the fast mode. In fact, anticipating what has been found at high densities, in that case the contribution of the fast mode to $S_{22}(k, \omega)$ is completely negligible, like here for low densities, but in $S_{11}(k, \omega)$ the contribution of other propagating modes is comparable to that of the fast mode. However, using the same method as here, namely leaving out the fast mode in the calculation of the $S_{ij}(k, \omega)$, the contribution of the fast mode to $S_{11}(k, \omega)$ is clearly visible for large ω . Finally, as far as the non propagating modes are concerned, one could explain that the contribution to the heavy component comes from the eigenvalue with the smaller (in absolute value) real part, by arguing that the heavy particles diffuse with more difficulty; in fact a smaller absolute value of the real part implies a slower decay of the corresponding mode.

c) Relevant to the previous point is the following, very important, observation. If we compute the group velocity associated with the fast mode,

we find that it is roughly constant in the relevant region in k , and we find a value which is very close (about 1 % difference) from the value of the sound velocity of the pure H_2 fluid, obtained by removing all the heavy Ar atoms. Computing the group velocity of the slowest propagating mode, we find a value about 20 % lower than that of the sound velocity of the simple Ar fluid obtained by removing the H_2 molecules. This is consistent with the statement at the beginning of point b), in the sense that it seems again that the two components behave as two simple fluids, each of them in the background of the other component; this more markedly for the light component.

d) The "separation" of the dynamics appears to be gradual as a function of k . Without reproducing tables similar to Table (4.1) for different values of k , I can say the following. If we compute the contribution of the discrete eigenvalues to the $S_{ij}(k, \omega)$ at a value of k , below which the kinetic propagating mode becomes fast (which is at $k\sigma_{12} \approx 0.005$), we find that a separation in two sets of modes, that contribute respectively to $S_{11}(k, \omega)$ and $S_{22}(k, \omega)$, does not occur. In addition, if we compute the contribution of the different modes to the $S_{ij}(k, \omega)$ for $k\sigma_{12} = 0.01$, a value half of that of Fig. (4.3), but for which the fast mode is already present, we find a sizeable contribution to $S_{11}(k, \omega)$ also from the slow propagating mode.

e) As was mentioned in subsection 4.3.2, when the amplitude of a given mode is complex, as is always the case for the propagating modes in kinetic theory, the corresponding Lorentzian is not a simple bell shaped curve. Here I give some details, in order to see what this implies for the fast mode. In particular, I want to explain why we are able to see a shoulder due to the fast mode, in spite of its large damping.

Writing again, as in section 4.3, $z=i\omega_0-\gamma$, where I recall that $\gamma>0$, and taking for definiteness ω_0 positive, (I have dropped the subscript n and the dependence on k, since they are irrelevant for this point), and, for the corresponding amplitude $A=a+ib$ (here I have also dropped the subscripts i,j, because the argument is valid for any $S_{ij}(k,\omega)$), we have that the corresponding Lorentzian is given by:

$$\text{Re} \frac{a+ib}{i(\omega-\omega_0)-\gamma} = \frac{a\gamma+b(\omega-\omega_0)}{(\omega-\omega_0)^2+\gamma^2} \quad (4.14)$$

The extrema of this curve are at the values:

$$\omega = \omega_0 + \frac{\gamma}{b} [-a \pm (a^2+b^2)^{1/2}] \quad (4.15)$$

If b is positive, the smaller value of ω is a minimum, while the larger is a maximum; and viceversa if b is negative. We see that γ is still roughly a measure of the range of the Lorentzian, if $|a|$ and $|b|$ are of the same order of magnitude. To have more quantitative arguments, consider the following situations, that give an idea of what (4.15) implies. If, for example, $b=a$, then (4.15) gives for the extrema:

$$\omega = \omega_0 + \gamma(-1 \pm \sqrt{2}) \quad (4.16)$$

If, on the other hand, $b=-a$, then the extrema are at:

$$\omega = \omega_0 + \gamma(1 \pm \sqrt{2}) \quad (4.17)$$

This last case corresponds to the situation which occurs, approximately, for the fast mode, as can be checked in Table (4.1) (I recall that a and b are, respectively, the real and imaginary parts of the amplitudes A). If γ is not larger than ω_0 , although, contrary to hydrodynamics, of the same order of magnitude, we still can talk of a maximum of the Lorentzian at, approximately, $\omega \approx \omega_0 - 0.4\gamma$ (which is the smaller of the two values in (4.17), where the maximum occurs, for $b<0$), reasonably displaced from the origin $\omega=0$

and from the other modes, if these have imaginary parts well below ω_0 . As I wanted to show, this also explains why we are able to see a shoulder corresponding to the fast mode, and why this shoulder is generally somewhat displaced towards the origin $\omega=0$, with respect to the value $\omega=\omega_0$. If γ is considerably larger than ω_0 then the range of the Lorentzian extends up to the origin, and the preceding argument does not hold. This happens also if b is considerably larger than a , and γ is roughly equal to ω_0 , as can be checked from (4.15). In these cases one can hardly speak of an observable propagating mode, either because, if $\gamma > \omega_0$, the damping is too large for a shoulder to be present, or, if $b > a$, the mode is not associated with a shoulder in $S_{ij}(k, \omega)$, but at most with a very slow decrease of this function from its value at $\omega=0$, resulting in a very broad Lorentzian. Concerning this last point, see also the next subsection, where I will study different relative concentrations of H_2 .

f) When it comes to experimental observation, the presence of the fast mode, could be deduced from the presence of an extended shoulder in $d^2\sigma/d\omega d\Omega$. Then it should be possible to deduce that it contributes only to $S_{11}(k, \omega)$ in the following way, although one can measure only $d^2\sigma/d\omega d\Omega$, and not the individual $S_{ij}(k, \omega)$. If we remove the H_2 molecules from the mixture and we compute $d^2\sigma/d\omega d\Omega$ for the pure Ar fluid so obtained, at the same k value as that of Figs. (4.3) and (4.4), we get a curve, shown in Fig. (4.5), which has a range practically identical to that of $S_{22}(k, \omega)$ in the mixture. This is reasonable in view of the previous points, where it was observed that the dynamics of the two components are approximately separate. If one trusts that the same would happen in a real mixture, then performing an experiment in pure Ar would give roughly the range of $S_{22}(k, \omega)$ in the H_2 -Ar

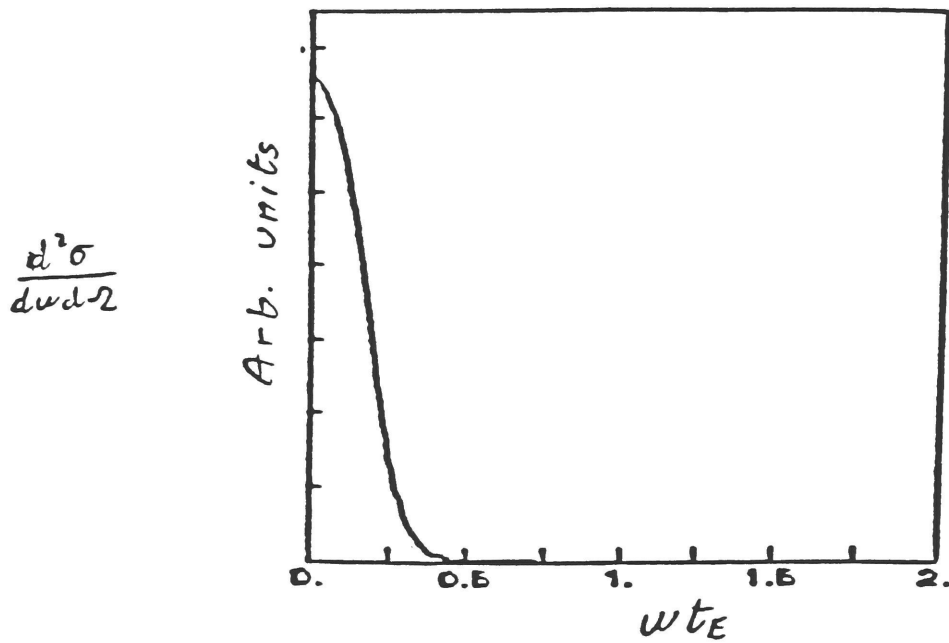


Fig. 4.5. $\frac{d^2\sigma}{d\omega d\Omega}$ for a pure Ar fluid obtained by removing the H_2 molecules from the mixture of Figs. (4.3) and (4.4). t_E and κ are the same as in that mixture.

mixture; if this range does not include the values for which $d^2\sigma/d\omega d\Omega$ has a shoulder, one could deduce that this shoulder must be in $S_{11}(k, \omega)$. As far as $S_{12}(k, \omega)$ is concerned, we see that it is smaller in absolute value than $S_{11}(k, \omega)$ and $S_{22}(k, \omega)$. This is usually the case in dilute mixtures, and it is to be expected, since the integral of $S_{12}(k, \omega)$ over the frequency gives $S_{12}(k)$, the static cross structure factor, which is a small quantity at low densities, since it is then proportional to n^* . Finally, that this extended shoulder is due to a fast mode could be deduced from the fact that its "center" is at a position, in ω , well above $\omega = c_s k$, where c_s is the velocity of sound.

g) There does not seem to be an analogous way to deduce, in an experiment, the presence of a low frequency and slow propagating mode whose contribution is mainly in $S_{22}(k, \omega)$. We note that presumably the central peak in $S_{22}(k, \omega)$ masks any possible shoulder at low frequencies.

This ends my remarks.

II $2M > 10$ approximations

The next question is what happens if we improve the approximation, i. e., if in the BGK method we increase M . To this purpose I show in Fig. (4.6) the $S_{ij}(k, \omega)$ obtained for $2M=20$ at the same value $k\sigma_{12}=0.02$ considered before. Except for a small difference in $S_{11}(k, \omega)$ for $\omega \approx 0$, the curves obtained are identical to those for $2M=10$ in Fig. (4.3); in particular the shoulder in $S_{11}(k, \omega)$ is unchanged. This gives confidence that the $S_{ij}(k, \omega)$ have already reached their asymptotic dependence on M for this k value at $2M=10$. The situation is very different for the modes. I show in Fig. (4.7)

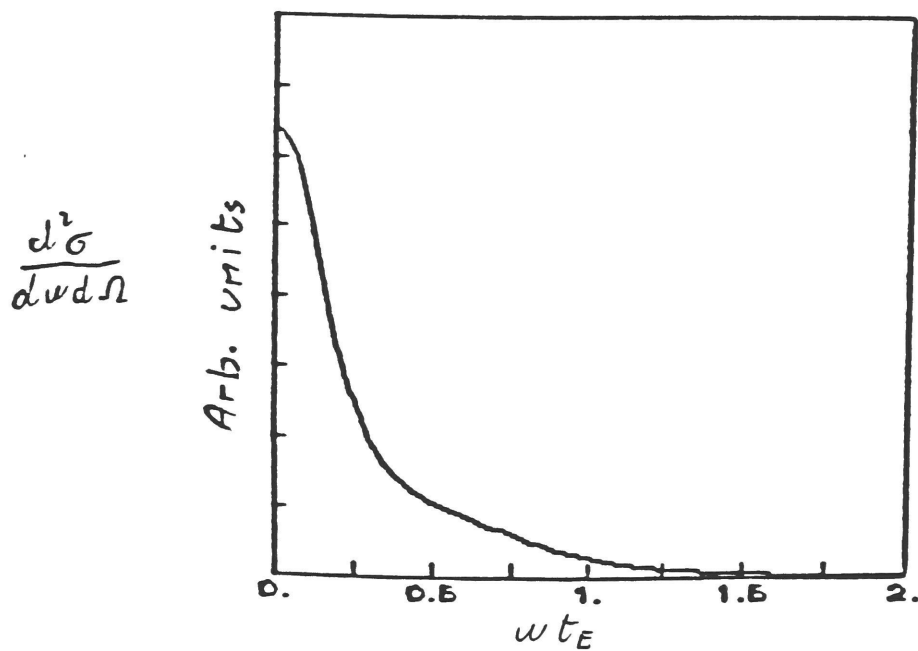
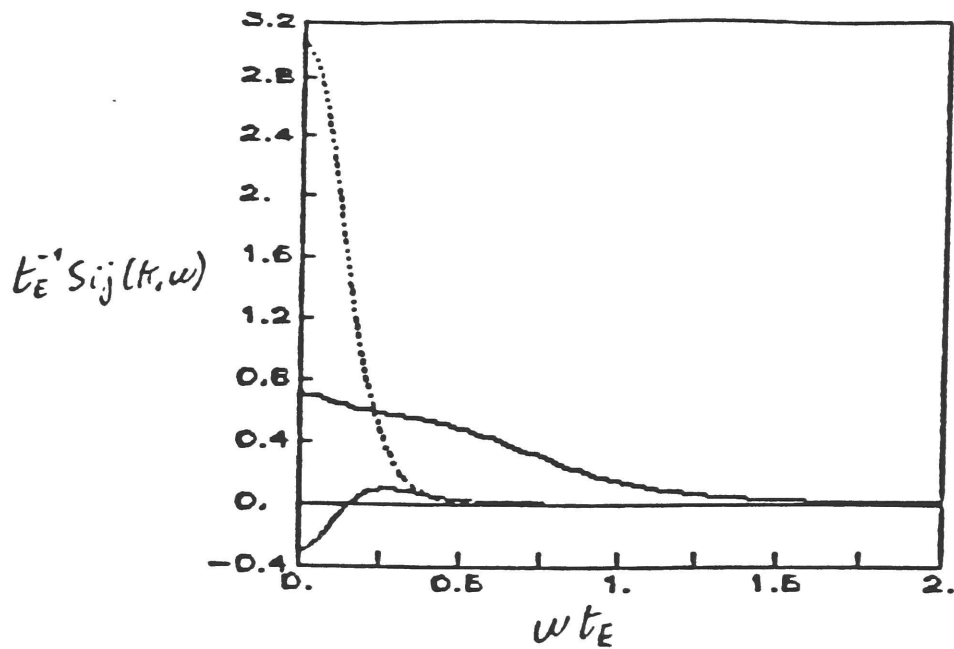


Fig. 4.6. Same as Fig. (4.3), but computed in the BGK approximation with $2M=20$.

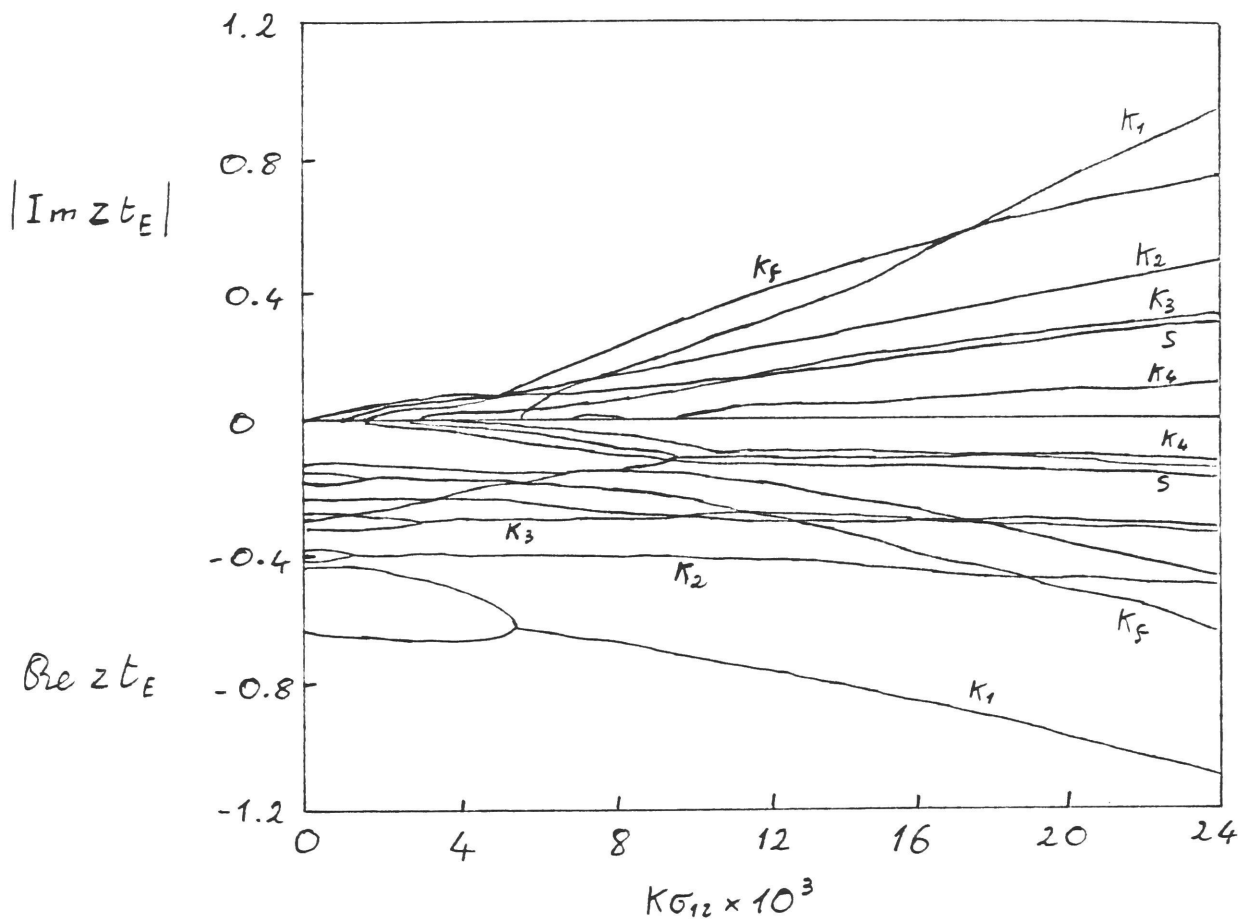


Fig. 4.7. 15 eigenvalues, obtained in the BGK approximation with $2\pi=20$, for H_2 -Ar with $n^*=0.005$ and $x_{H_2}=0.8$. With K_f I have indicated the eigenvalue associated with the "relevant" fast mode (see text). Also indicated with characters are the eigenvalues associated with the other propagating modes: the extended sound mode (s) and the kinetic modes ($K_i, i=1,2,3,4$).

15 eigenvalues. We see that not only there are more propagating modes, but that two of them become fast at roughly the same value, around $k\sigma_{12}=0.005$, which is the same as in the case $2M=10$. Then one could say that there are two fast propagating modes. However, first, if one computes the $S_{ij}(k,\omega)$ using 15 discrete eigenvalues, one obtains curves identical to those of Fig. (4.6). Secondly, computing the amplitudes of the different eigenvalues, one sees that the two fast modes only contribute to $S_{11}(k,\omega)$, and one of the two has an amplitude, for $S_{11}(k,\omega)$, considerably larger than the other. Therefore there is only one relevant fast mode.

I end this subsection with the following conclusions.

a) The $S_{ij}(k,\omega)$ are stable with respect to an increase of the number M , when $2M \geq 10$; thus one has some confidence that if one could (and would) use a very large M one would obtain the same results.

b) The modes themselves change with M . But the important point is that there is always a fast propagating mode that contributes only to the dynamics of the light component. Besides, the eigenvalue associated with the fast mode changes very little with M .

c) One is then led to the conclusion that in the case $2M=10$ the dynamics, that should in principle be described with $M \rightarrow \infty$, is already correctly computed (at least the dynamics of the density-density correlation functions $S_{ij}(k,\omega)$).

The last remarks lead us to the effective mode description. The mathematics of this approach is briefly explained in Appendix II. Here I will just say the following about the physical meaning of the procedure. In the effective mode approach one takes a given value of $2M$, say $2M=20$. Then it is assumed that the time decay of the correlation functions between

polynomials $\phi_{\ell}^{(i)}(\vec{v})$, with $i=1,2$ and $\ell=M'+1, M'+2, \dots, M$ ($M' < M$), is much faster than that of the other correlation functions. As a result, through a procedure which is outlined in Appendix II, one gets then $2M'$ effective modes, and an approximation of the $S_{ij}(k, \omega)$ with $2M'$ Lorentzians. In Fig. (4.8) I show the 8 effective modes ($2M'=8$) obtained from $2M=20$. There are only two propagating modes. One corresponds to the extended sound mode, and the other starts propagating at a value not too different from $k\sigma_{12}=0.005$ (the same value for which in $2M=10$ and $2M=20$ one mode becomes fast propagating), and it is fast as soon as it begins to propagate. If we compute the $S_{ij}(k, \omega)$ in this approximation, for the same value $k\sigma_{12}=0.02$ as before, we get curves that are indistinguishable from those obtained for $2M=20$. Therefore the 8 effective modes suffice in the calculation of the $S_{ij}(k, \omega)$. In Table (4.2) I give the effective modes, i. e., the eigenvalues and the corresponding amplitudes. Again, the fast mode contributes only to $S_{11}(k, \omega)$.

On the basis of the effective mode description one can argue that the modes in the BGK approximation with $2M=10$ effectively describe the dynamics of the fluid, at least as far as the dynamics of the $S_{ij}(k, \omega)$ is concerned.

4.5.2 Other relative concentrations

In this subsection I present the results obtained for relative concentrations other than $x_1=0.8$. I will give less details than in the previous subsection; in particular I will restrict myself to the BGK approximation with $2M=10$, since we have learned that the observable

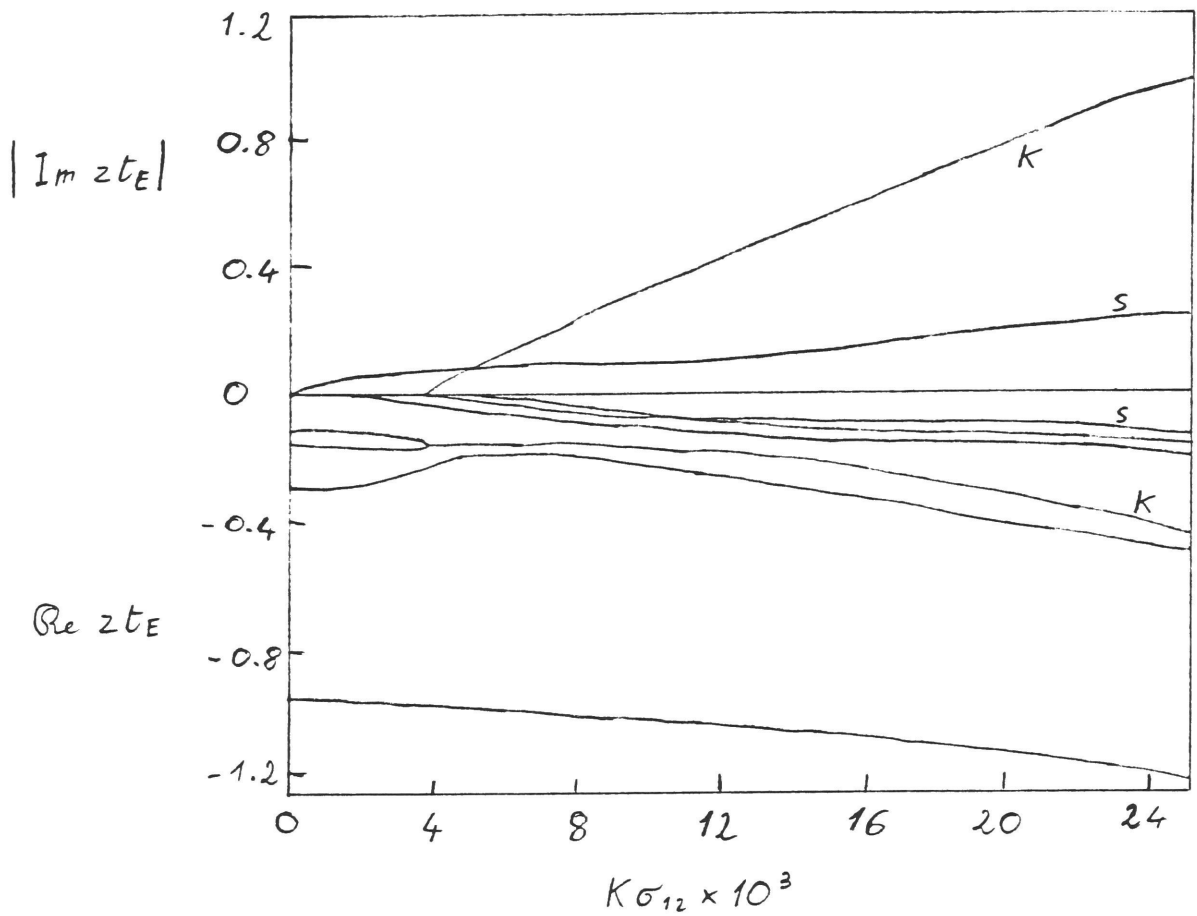


Fig. 4.8. 8 effective eigenvalues in H_2 -Ar with $n^*=0.005$ and $X_{H_2}=0.8$. I have marked with characters the eigenvalues associated with propagating modes: the extended sound mode (s), and the kinetic fast mode (k).

TABLE 4.2

Amplitudes A_{ij} for the $S_{ij}(k, \omega)$, corresponding to the 8 effective eigenvalues of Fig. (4.8), for $k\sigma_{12} = 0.02$. Here the eigenvalues associated with propagating modes are indicated with the same characters as in Fig. (4.8).

Eigenvalue	A_{11}	A_{22}	A_{12}
$-0.111 + 0.192i$ s	$-0.019 + 0.010i$	$0.104 - 0.300i$	$0.062 + 0.054i$
$-0.111 - 0.192i$ s	$-0.019 - 0.010i$	$0.104 + 0.300i$	$0.062 - 0.054i$
-0.116	0.010	0.479	-0.087
-0.319	0.402	0.001	-0.021
-0.156	0.004	0.011	0.007
$-0.404 + 0.758i$ k	$0.253 - 0.307i$	$-10^{-4} + 3 \times 10^{-4}i$	$-0.010 - 0.006i$
$-0.404 - 0.758i$ k	$0.253 + 0.307i$	$-10^{-4} - 3 \times 10^{-4}i$	$-0.010 + 0.006i$
-1.134	0.116	2×10^{-5}	-0.002

quantities, $S_{ij}(k, \omega)$, seem to be quite insensitive to an increase in the number M .

In Fig. (4.9) we see 8 eigenvalues for the relative concentration $x_{H_2}=0.9$, and for the relative concentration $x_{H_2}=0.6$. They differ in some respects from the eigenvalues for $x_{H_2}=0.8$. For the relative concentration 0.9 it is the extended sound mode, rather than a kinetic mode, that, for a value of $k\sigma_{12}$ around 0.005, increases its slope, so that it begins to propagate faster. Correspondingly, the damping of the extended sound becomes larger than that of the other modes. The values of $k\ell_1$ and $k\ell_2$ corresponding to $k\sigma_{12}=0.005$ are, respectively, 0.218 and 0.053. On the other hand, for the relative concentration 0.6 a kinetic mode begins to propagate at about $k\sigma_{12}=0.006$, and it propagates fast from the beginning. The corresponding values for $k\ell_1$ and $k\ell_2$ are increased to 0.356 and 0.106, respectively. Also in this case the damping of the fast propagating mode is larger than that of the other modes. In both cases the group velocity of the fast mode is very close to the velocity of sound of the pure H_2 fluid obtained removing the Ar atoms. Actually, for the case $x_{H_2}=0.6$, the fast mode, soon after it begins to propagate at $k\sigma_{12}\approx 0.006$, has an even larger slope than for larger k . But in that small region, soon after it begins to propagate, the imaginary part of the corresponding eigenvalue is small, so that it cannot give rise to a side shoulder.

If, for both the concentrations $x_{H_2}=0.6$ and $x_{H_2}=0.9$, we compute the $S_{ij}(k, \omega)$ using only the discrete modes, which, again, give curves identical to those obtained by matrix inversion, we see that the fast mode, again,

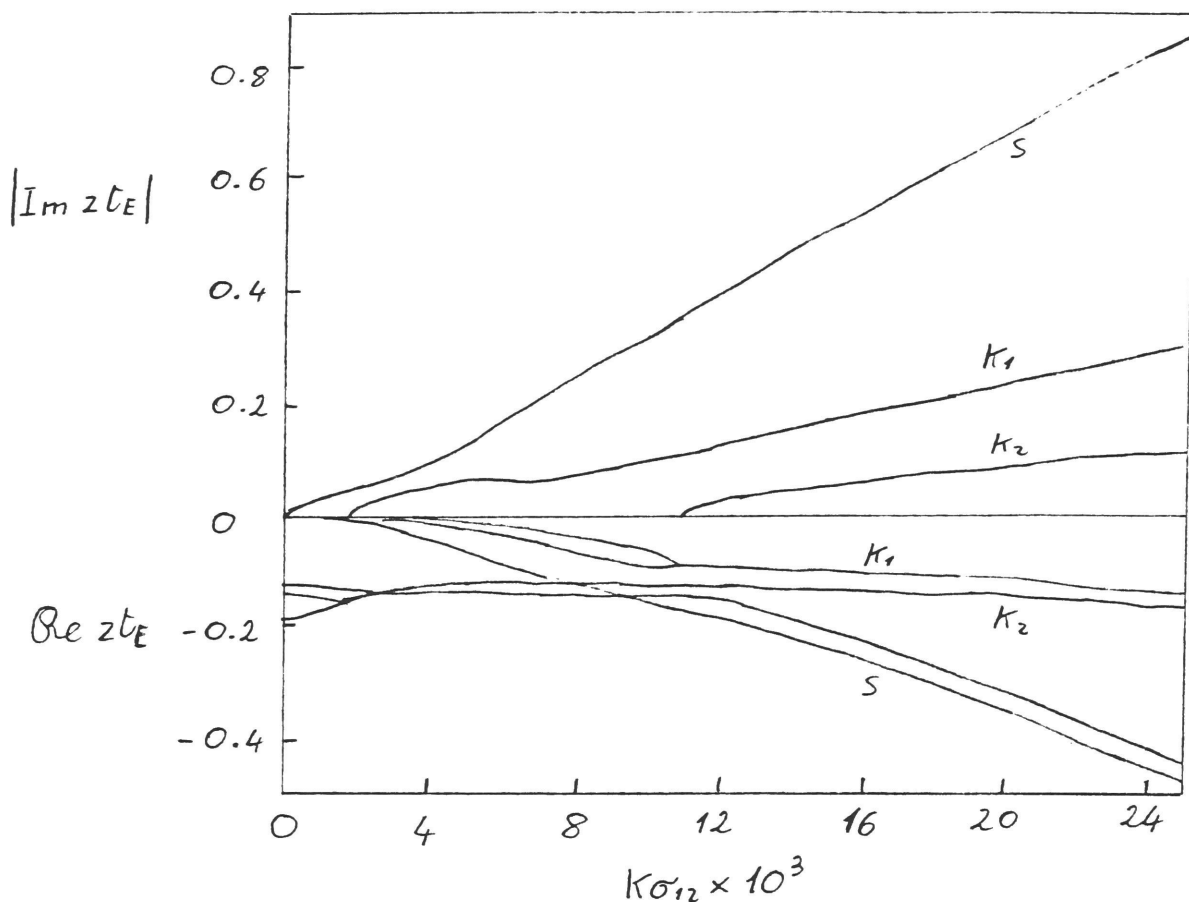


Fig. 4.9 a). 8 eigenvalues for H_2 -Ar with $m^*=0.005$ and $X_{H_2}=0.9$. The extended sound mode (the corresponding eigenvalue is marked with s) becomes fast propagating for $k\sigma_{12} \approx 0.005$. The characters κ_1 and κ_2 mark the other eigenvalues corresponding to propagating modes.

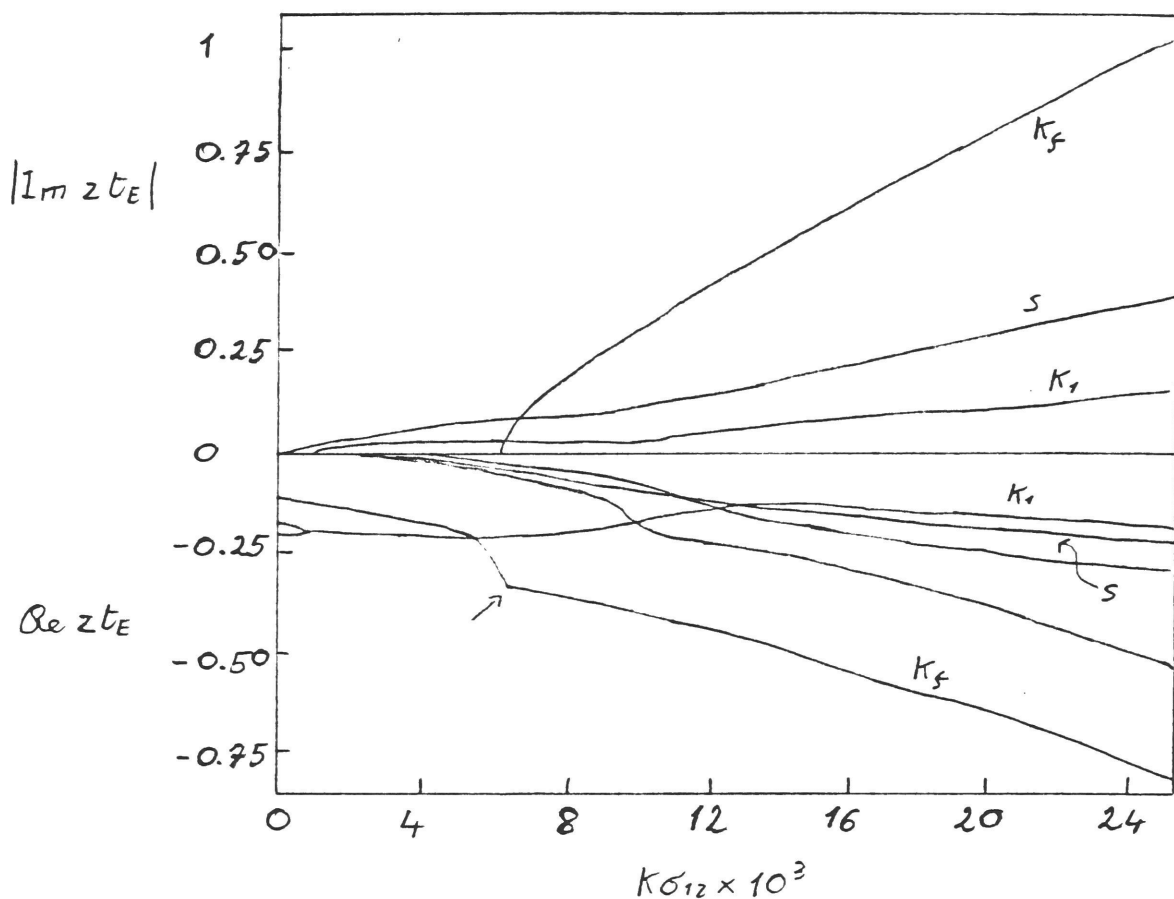


Fig. 4.9 b). 8 eigenvalues for H₂-Ar with $\pi^* = 0.005$ and $X_{H_2} = 0.6$. K_f marks the eigenvalue associated with the fast mode. It begins to propagate at $K\sigma_{12} \approx 0.006$; not shown is the real eigenvalue that, at the point indicated by the arrow, becomes equal to the other real eigenvalue (the curve marked with K_f for values of $K\sigma_{12}$ smaller than that corresponding to the arrow) to give rise to the fast propagating eigenvalue. Although not explicitly stated there, the same situation occurs in some of the following figures. s and K_1 mark the eigenvalues associated with the und and a kinetic propagating mode.

contributes practically only to $S_{11}(k, \omega)$. I do not reproduce the figures here.

Comparison of these two cases, $x_{H_2}=0.9$ and 0.6 , and the one with $x_{H_2}=0.8$ already allows to draw some conclusions. The fast mode, at the different concentrations, is always a mode that propagates at a velocity very close to the the velocity of sound of the pure H_2 fluid obtained removing the Ar atoms from the mixture, and it always contributes only to $S_{11}(k, \omega)$. It is always a mode with a large damping compared to the other modes. However, the damping is not so large to prevent the appearance of a shoulder in $S_{11}(k, \omega)$ (cf. remarks below expression (4.17)). The values of $k\ell_1$ and $k\ell_2$, for which the fast mode appears, increase if the relative concentration of H_2 decreases. This means that the "separation" of the dynamics of the two components begins at a shorter wavelength, compared to the mean free paths ℓ_1 and ℓ_2 , if the relative concentration of H_2 is decreased. We can take $x_{H_2}=0.9$ as a sort of upper limit for the relative concentration of H_2 , in order for the fast mode to exist. This because if we increase x_{H_2} further the sound velocity of the mixture will approach closely the sound velocity of the pure H_2 fluid, and therefore there will be no jump in the slope of the extended sound mode.

Now I want to investigate what the lower limit for x_{H_2} is. In Fig. (4.10) I have plotted 8 eigenvalues for values of x_{H_2} equal to 0.4 and 0.3 . Like for $x_{H_2}=0.6$ there is a fast mode that is fast as soon as it begins to propagate. Again its group velocity is very close to the sound velocity of the pure H_2 fluid. The trend mentioned before, on the increase of the values

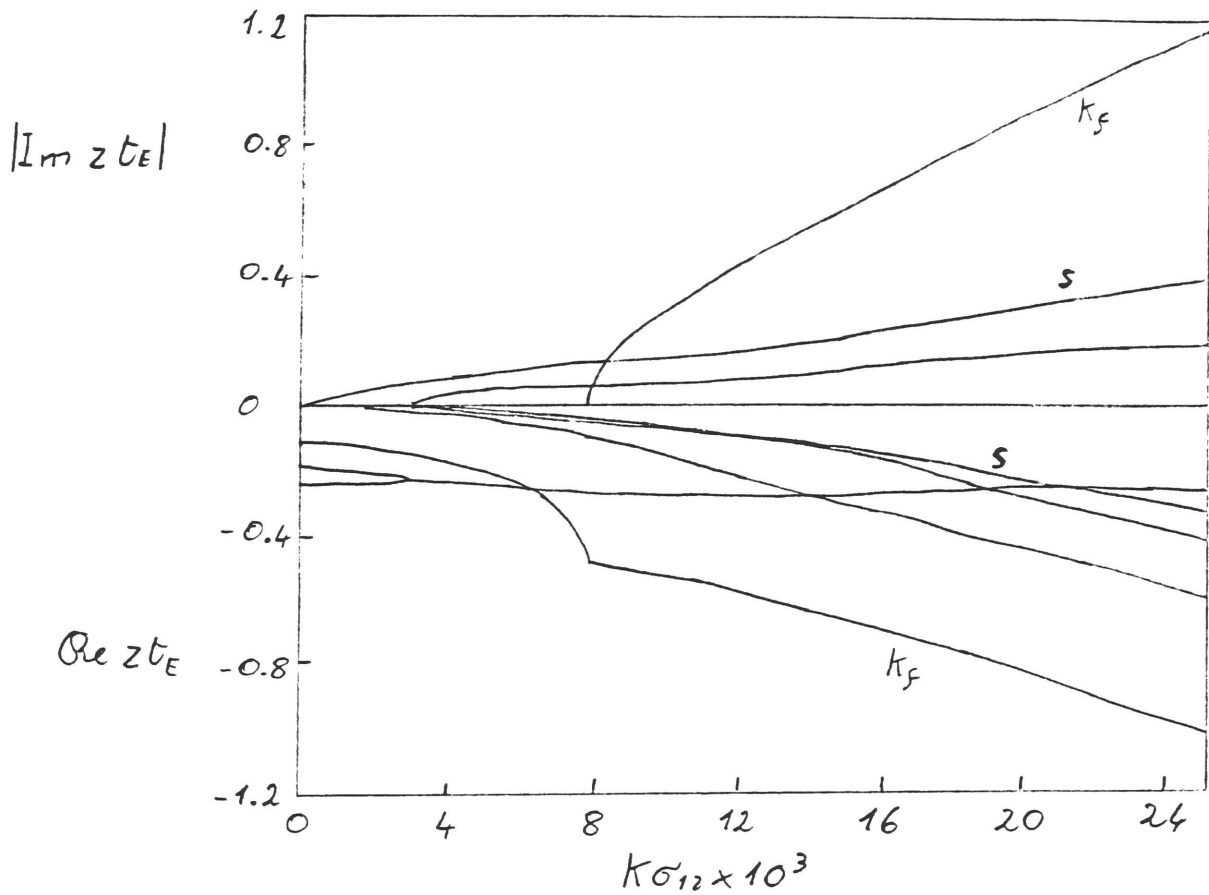


Fig. 4.10 a). 8 eigenvalues for H_2 -Ar with $\eta^* = 0.005$ and $X_{H_2} = 0.4$. s and k_f indicate the eigenvalues associated with the extended sound mode and with the fast propagating mode, respectively.

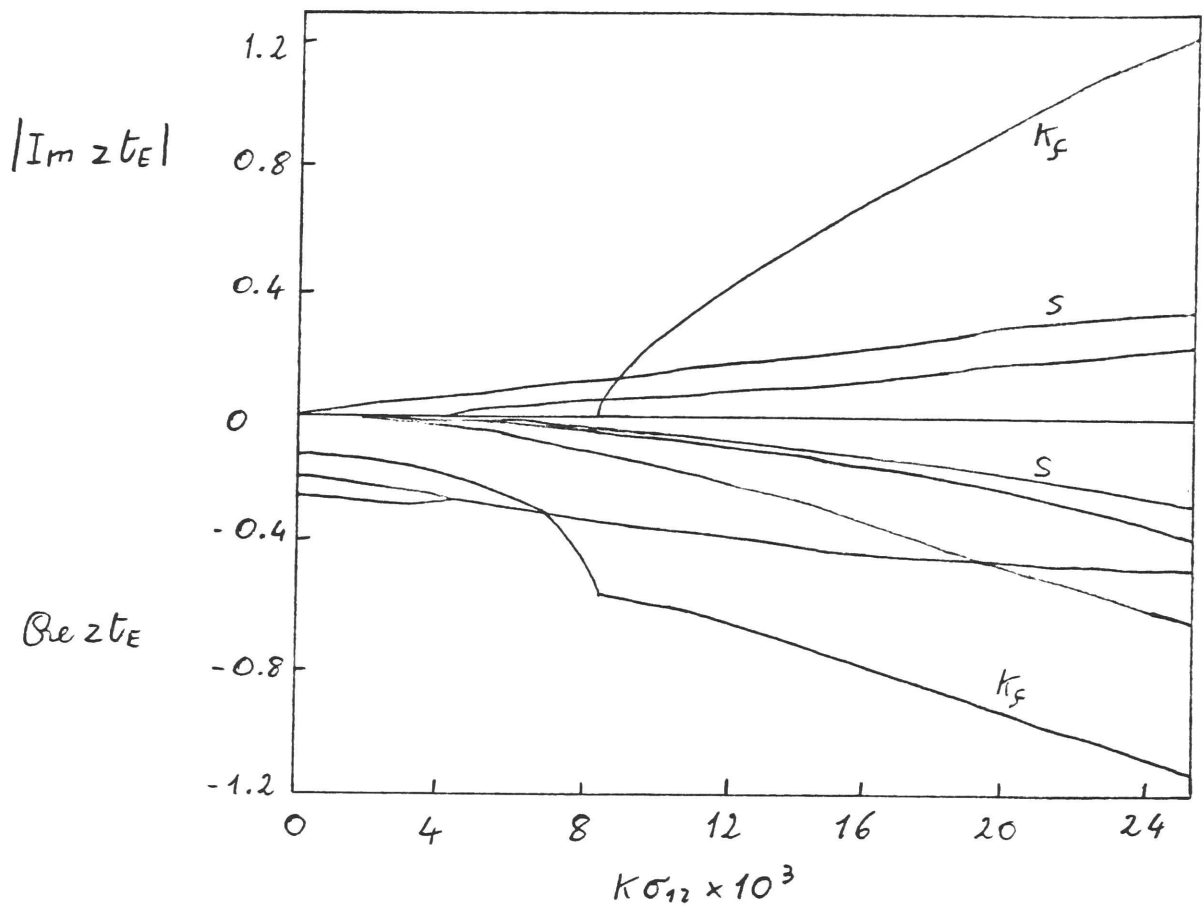


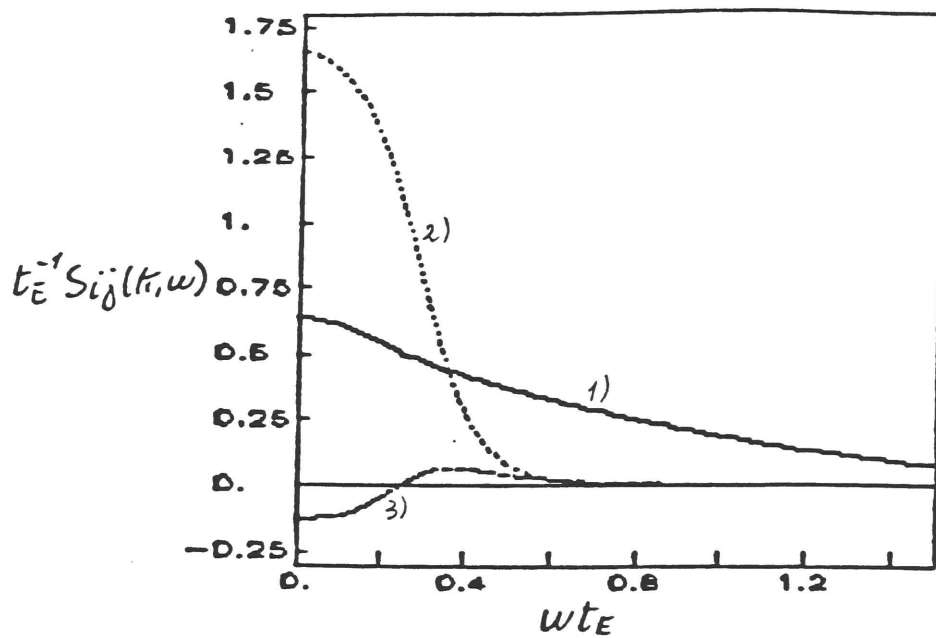
Fig. 4.10 b). 8 eigenvalues for H_2 -Ar with $\pi^* = 0.005$ and $X_{H_2} = 0.3$. s and k_f like in a).

of $k\ell_1$ and $k\ell_2$ for which the fast mode appears, is confirmed, because for the relative concentration 0.4 the values are 0.560 and 0.197 respectively, while for the relative concentration 0.3 they are 0.603 and 0.234 respectively.

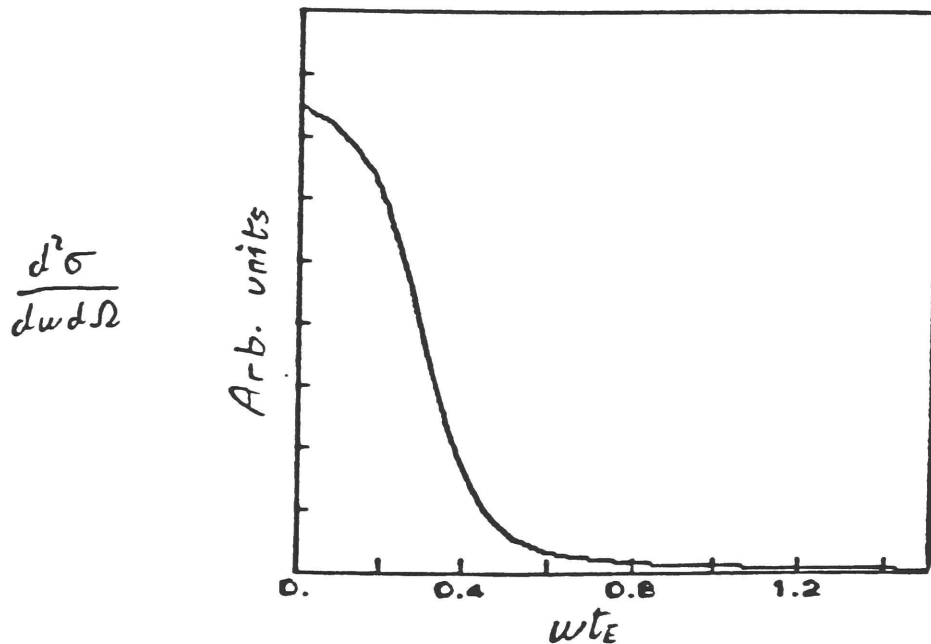
However, let me consider the $S_{ij}(k, \omega)$ for $x_{H_2}=0.3$ and $k\sigma_{12}=0.02$. They are plotted in Fig. (4.11). Again matrix inversion and 8 discrete eigenvalues give the same curves. We see that now we cannot really talk about a shoulder in $S_{11}(k, \omega)$, but only of a very slow decrease of $S_{11}(k, \omega)$, which is practically not reflected in $d^2\sigma/d\omega d\Omega$ (since x_{H_2} is smaller than in the previous cases, the relative weight of $S_{11}(k, \omega)$ is smaller). This is related to what was observed at the end of point e) in part I of the previous subsection. In fact, without reproducing another table of amplitudes, I just mention the amplitude of $S_{11}(k, \omega)$ corresponding to the fast mode: it is $0.184-0.341i$. As we see, the imaginary part is, in absolute value, almost twice as much as the real part, and this causes the Lorentzian corresponding to this eigenvalue to become very broad. So for this low concentration we can hardly speak of a fast propagating mode. Moreover, in $d^2\sigma/d\omega d\Omega$ the slow decrease of $S_{11}(k, \omega)$ is not observable. Therefore we can take as a lower limit for x_{H_2} , in order for an observable fast mode to be present, a value around 0.4.

4.5.3 A summary

In this section I have shown, in dilute H_2 -Ar mixtures, the characteristics of the fast mode. We have seen that by varying the



a)



b)

Fig. 4.11. a) $S_{ij}(k, \omega)$ for H_2 -Ar with $n^* = 0.005$ and $x_{H_2} = 0.3$. The value of $K\sigma_{12}$ is 0.02: 1) $= S_{11}(k, \omega)$; 2) $= S_{22}(k, \omega)$; 3) $= S_{12}(k, \omega)$. b) The differential scattering cross section.

concentration some details change: at high (0.8) H_2 concentration the fast mode is a kinetic mode that begins to propagate slowly for a rather small value of k , and, at a certain value of k , its slope has a jump and the mode becomes fast propagating. For even higher H_2 concentration it is the extended sound mode that, for a given k , has a jump in the slope and begins to propagate fast, until, for concentrations higher than about 0.9, this jump is small and we cannot talk of a fast mode anymore. For lower H_2 concentrations the fast mode is a kinetic mode that, as soon as it begins to propagate, is fast. The values of $k\ell_1$ and $k\ell_2$, for which a fast propagating mode appears, increase if the relative concentration of H_2 decreases.

Other details are common to the different concentrations. The fast mode always contributes only to $S_{11}(k, \omega)$. Although it is always largely damped it appears in $S_{11}(k, \omega)$ as a visible shoulder. However, if the relative concentration of H_2 is too low, less than 0.4, there is no shoulder in $S_{11}(k, \omega)$. This is associated with an amplitude of the fast mode, corresponding to $S_{11}(k, \omega)$, that has an imaginary part considerably larger than the real part. This results in a very broad Lorentzian which causes the slow decrease in $S_{11}(k, \omega)$.

We have seen that if we increase the number M , which determines the order of the BGK approximation, we get a more complicated picture for the eigenvalues. However, the $S_{ij}(k, \omega)$ seem to be almost insensitive. We have also found that, although there are two modes that propagate fast, when $2M=20$, only one contributes, and only to $S_{11}(k, \omega)$. Then, there is always one "visible" fast propagating mode. Therefore, from this point of view, also the picture of the relevant modes has not changed appreciably from the case $2M=10$. As a confirmation of this point we have considered the so called

effective modes, obtained from $2M=20$ neglecting the decay time of the correlation functions concerning the polynomials with the highest indices.

4.6 Other mixtures

In this section I show some results for other mixtures, where the masses are less different.

In Fig. (4.12) we see the 8 eigenvalues obtained with the BGK approximation $2M=10$, for a H_2 -Ne mixture and a He-Ne mixture, respectively. The reduced density is $n^*=0.005$, and the relative concentration of the light component (H_2 and He respectively) is 0.6. In atomic units the mass of He is 4.003, and the mass of Ne is 20.183. Their diameters are taken to be $\sigma_{He}=2.17 \text{ \AA}$ and $\sigma_{Ne}=2.602 \text{ \AA}$. Therefore in the H_2 -Ne mixture the mass ratio is about 10, and in the He-Ne mixture it is about 5. For the polarizabilities we have $\alpha_{Ne} \approx 2\alpha_{He} \approx 0.52\alpha_{H_2}$, therefore they are all comparable.

We see that in both cases there is a mode that begins, at a certain value of k , to propagate faster. If we compute its group velocity, we again find that it is very close to the velocity of sound of the pure fluid obtained removing the heavier atoms. Therefore still for a mass ratio around 5 we can talk of a fast mode, although the difference in slopes between the fast mode and the sound is smaller. In Fig. (4.13) we see the $S_{ij}(k, \omega)$ and the $d^2\sigma/d\omega d\Omega$ for He-Ne for $k\sigma_{12}=0.04$. Now, as we expect, the difference in range between $S_{11}(k, \omega)$ and $S_{22}(k, \omega)$ is smaller; besides, the position of the shoulder in $S_{11}(k, \omega)$, attributed to the fast mode, is close to the position of the peak in $S_{12}(k, \omega)$ (although this peak is very small, since, as noticed in point f) in part I of subsection 4.5.1, $S_{12}(k, \omega)$ itself is small,

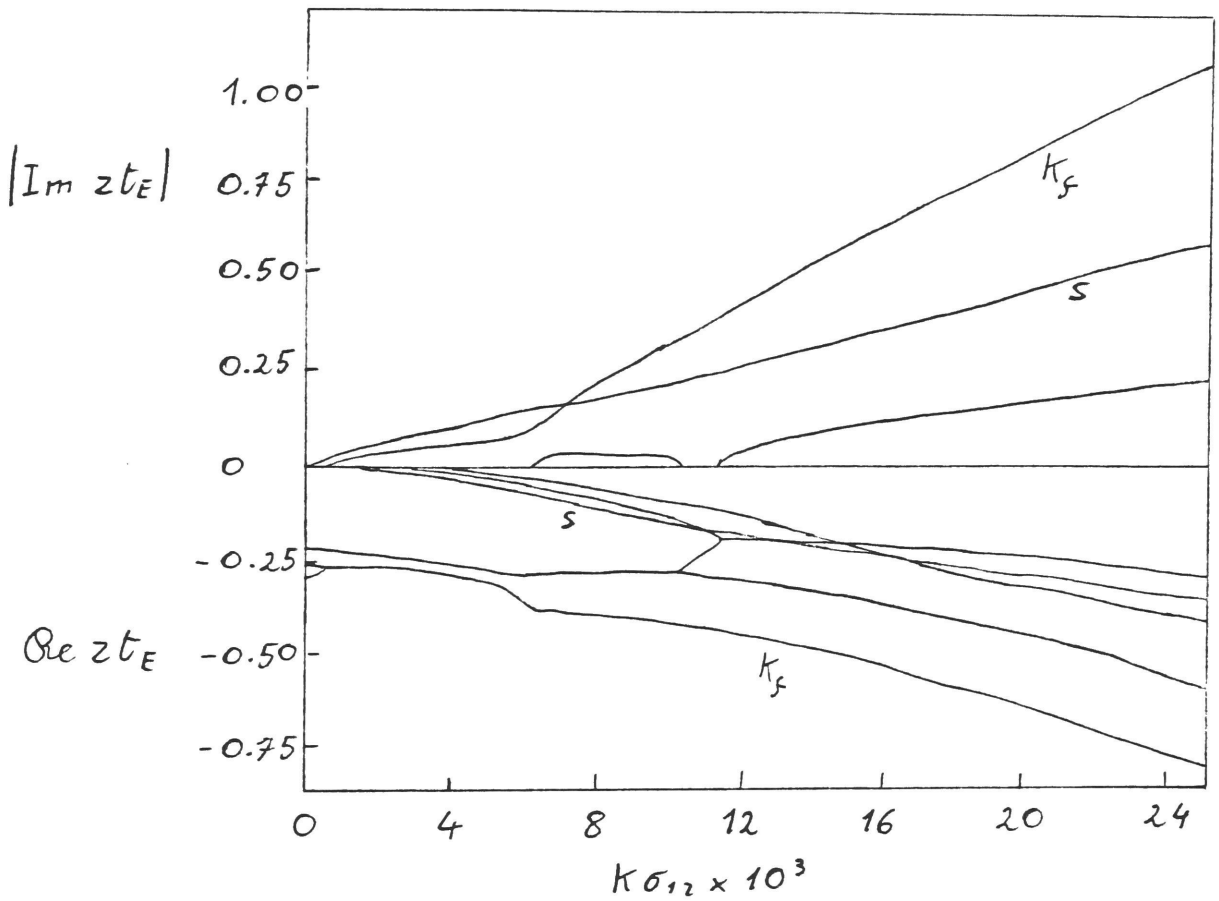


Fig. 4.12 a). 8 eigenvalues for H_2-Ne with $\pi^*=0.005$ and $X_{H_2}=0.6$. s and k_f like in Fig. (4.10a).

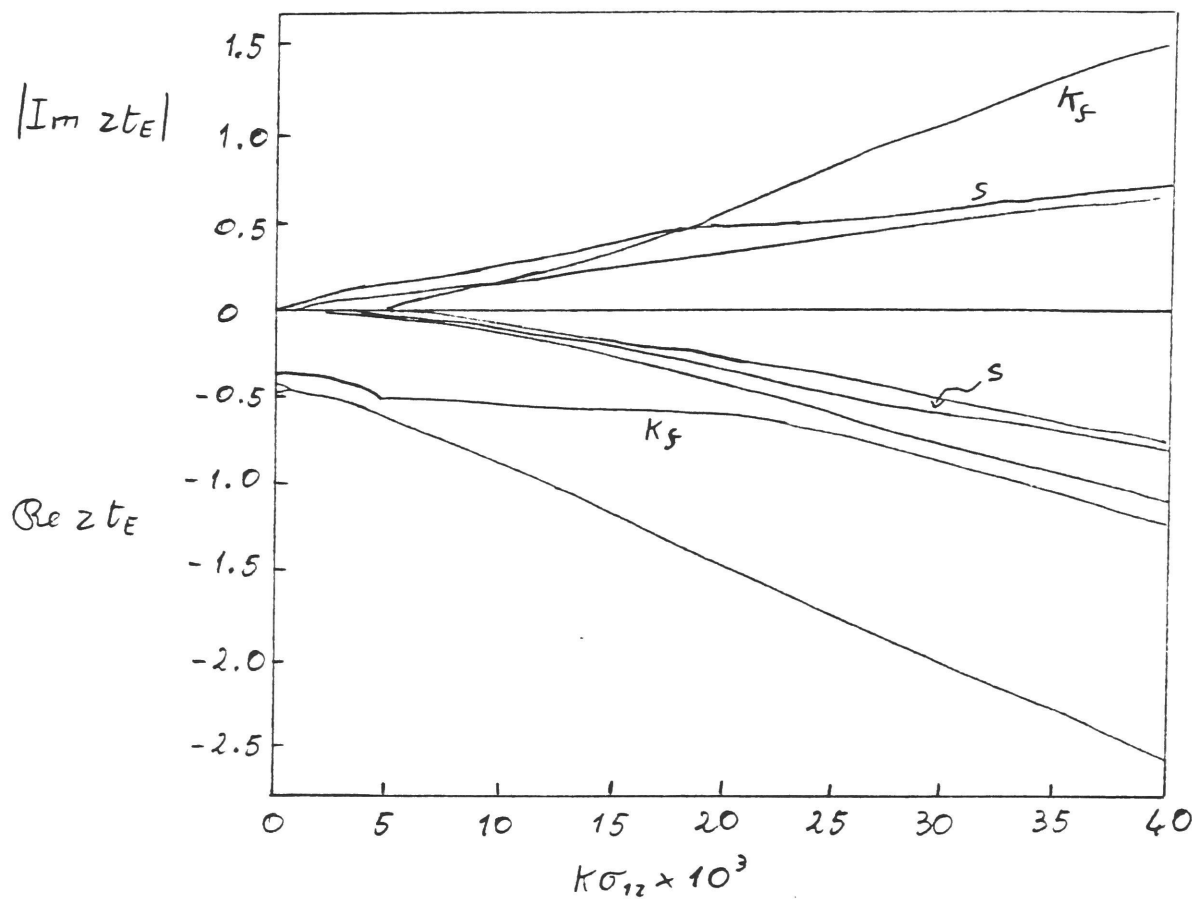
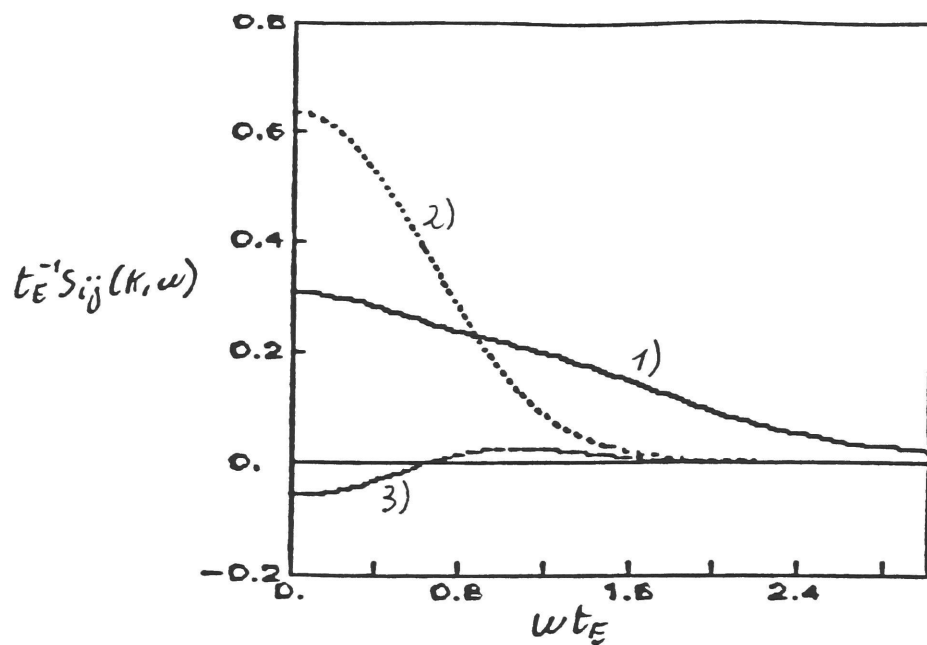
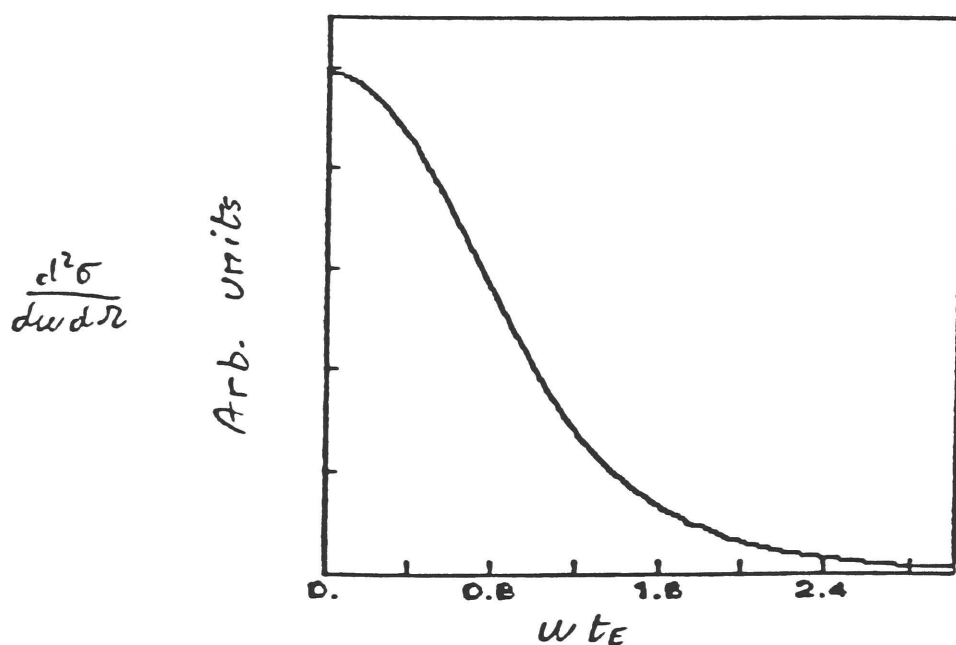


Fig. 4.12 b). 8 eigenvalues for He-Ne
with $n^* = 0.005$ and $X_{\text{He}} = 0.6$. s and κ_f
like in Fig. (4.10a).



a



b)

Fig. 4.13. a) $S_{ij}(k, \omega)$ for He-Ne with $n^* = 0.005$ and $x_{He} = 0.6$. The value of $k\sigma_n$ is 0.04: 1) $= S_{11}(k, \omega)$, 2) $= S_{22}(k, \omega)$; 3) $= S_{12}(k, \omega)$. b) The differential scattering cross section.

compared to $S_{11}(k, \omega)$ and $S_{22}(k, \omega)$, in dilute mixtures), indicating that now the fast mode makes also a sizeable contribution also to $S_{12}(k, \omega)$. We will see that for higher densities the fast mode does not appear for such, not very large, mass ratios.

4.7 Dense fluids: neutron scattering

4.7.1 Introduction

For dense fluids the only available kinetic theory is that for hard spheres. However, in dense fluids, where the reduced density n^* is of order 1, one can raise more objections, than in dilute fluids, about the validity of the hard-sphere approximation in representing real fluids. The reasons are obvious. It is expected that in dense fluids with realistic potentials one particle is in the range of influence of more than just another particle, so that there are collisions that are not binary, but involve more than two particles. Besides, neglect of an attractive part in the potential is also an important factor. If the temperature of the fluid is such that the average kinetic energy of a particle is large compared to the depth of the attractive part of the real potential, then it is expected that the interaction resembles a hard sphere interaction, since the particles will interact significantly only through the steep repulsive part of the potential, which is close to a hard sphere potential. Of course the best check of the reliability of the hard sphere approximation lies in the experiments. The indications in this sense are encouraging. For a comparison of the results of the hard sphere kinetic theory for simple fluids with the

experimental results of neutron scattering on liquid argon, see, for example, de Schepper and Cohen¹²⁾.

The hard sphere diameter to assign to a given atom in a dense fluid is determined in the following way, which is different from the method used for dilute fluids. After explaining the procedure followed for dense fluids, I will say why the method is different from that followed for low densities. In a simple dense fluid the structure factor $S(k)$ has a characteristic shape, which is very similar for hard spheres and for a noble gas-like fluid, as found experimentally. In Fig. (4.14) I show $S(k)$ for a simple hard sphere fluid computed from the Percus-Yevick equation (cf. Chapter 3). We see that $S(k)$ has its principal maximum for $k\sigma$ around 6 ($k\sigma=2\pi$ corresponds to a wavelength $\lambda=2\pi/k=\sigma$). The $S(k)$ found experimentally for liquids of noble gases is very similar, and the equivalent hard sphere diameter σ is chosen such that the position of the first, principal, maximum of $S(k)$ corresponds to the position of the same maximum in the experimental curve [5]. The values found in this way for simple fluids are then also used in the mixtures. The reason to follow a different method for dense fluids is that this method, of fitting the position of the maximum of $S(k)$, is more precise, for dense fluids, than comparing, like in dilute fluids, the experimental viscosity (or another transport coefficient) with that found on the basis of the Enskog theory. This is because for dense fluids the transport coefficients computed on the basis of the Enskog theory differ somewhat from the "true" transport coefficients of a hard sphere fluid, as computed in computer simulation (for a comparison of Enskog theory with computer simulation of hard sphere fluids, see Ref. 5).

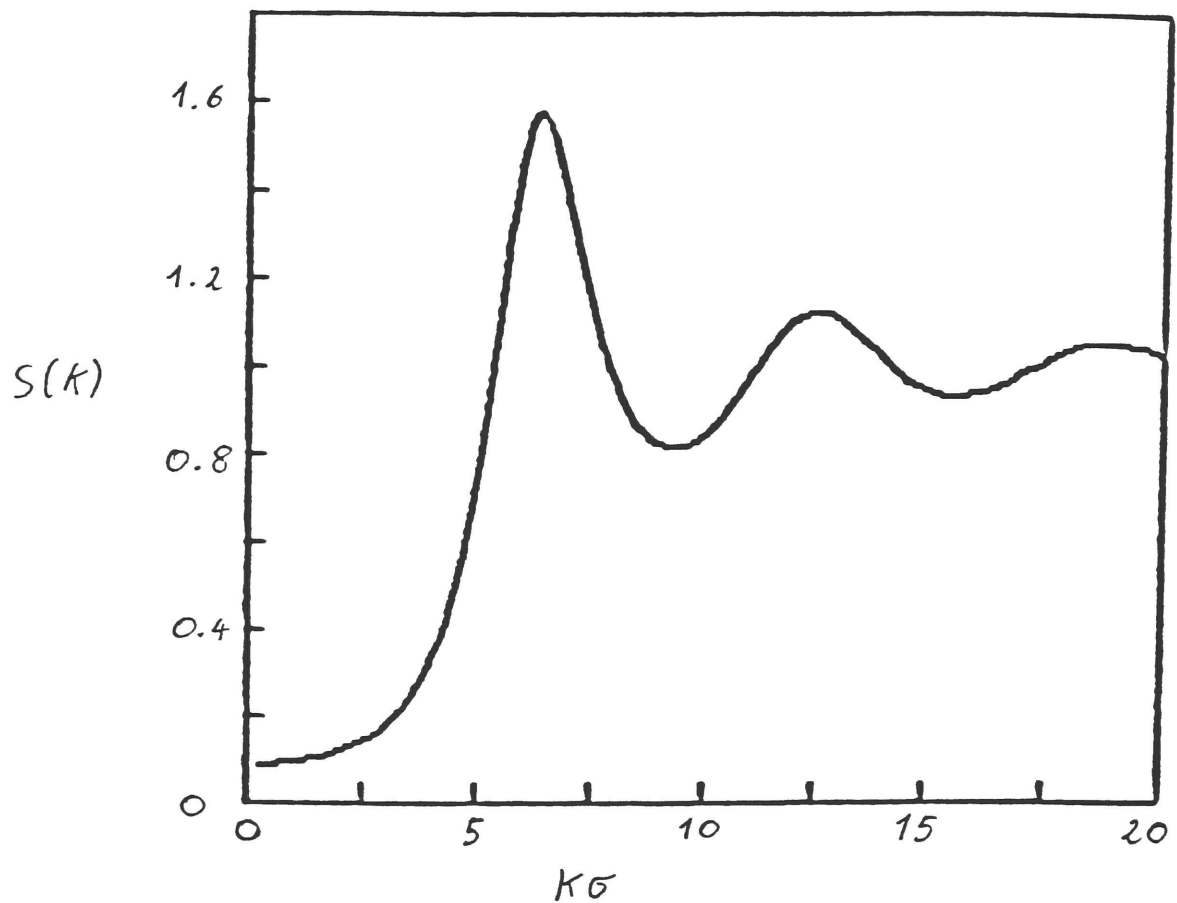


Fig. 4.14. $S(k)$ of a simple hard sphere fluid, computed with the Percus Yevick equation. The density is $\pi\sigma^3=0.6$.

4.7.2 A computer simulation on a liquid alloy

Recently a paper by Bosse et al.¹⁷⁾ presented a computer simulation of a liquid alloy Li-Pb at a temperature of 1085 °K. The mass of Pb is about 30 times that of Li. The relative concentration of Li was 0.8. In the $S_{\text{Li-Li}}(k, \omega)$ they found a side peak which was not present in $S_{\text{Pb-Pb}}(k, \omega)$ and $S_{\text{Li-Pb}}(k, \omega)$. As interaction potential they used a screened Coulomb potential plus a short range repulsion, characterized by the same length for both components. To analyze their "experimental" results the authors employed the Mori-Zwanzig formalism²⁰⁾. In the approximation they used, they obtained two undamped propagating modes. Of course this approximation cannot be used when $k \rightarrow 0$, because we know that there is then only one propagating mode, the sound mode. In addition, they ignored the damping of the modes. However, they argued that beyond the hydrodynamic regime this approximation improves. Thus they found two dispersion curves $\omega_1(k)$ and $\omega_2(k)$. The value of $\omega(k)$ corresponding to the peak in $S_{\text{Li-Li}}(k, \omega)$ corresponded approximately to the value of the largest of $\omega_1(k)$ and $\omega_2(k)$, say $\omega_1(k)$. They found that the slope of $\omega_1(k)$ at the lowest value of k they could study gave a velocity of propagation about three times higher than the velocity of sound. They called this mode fast sound. They could not investigate what happens when $k \rightarrow 0$, due to the usual size restrictions of the system in a computer simulation.

4.7.3 Density dependence

In dense fluids the mean free paths are of order 10^{-8} cm, the same order of magnitude of the diameters σ_1 , σ_2 and of the average interatomic

distance; actually, in general, the mean free paths are smaller than the diameters. Therefore, investigating a range of k associated with a wavelength of the same order of the mean free paths, we cannot ignore the k dependence of the collision operator, as can be done in dilute mixtures. This k -dependence is through $k\sigma_1$, $k\sigma_2$, $k\sigma_{12}$ (cf. Chapter 3), which now are not small compared to 1. Also the mean field operator is important at these densities.

So we should not expect, as in dilute mixtures, a simple scaling behavior with the density; at the same relative concentration of the two components, the results will change with the density. In other words, size effects are important, because at high density the spheres occupy a significant fraction of the total volume. However, we will also find many similarities with dilute mixtures.

4.7.4 Scattering lengths

In neutron scattering experiments the weighting factors, in the expression of the differential scattering cross section in terms of the $S_{ij}(k, \omega)$, are the scattering lengths b_1 , b_2 , of the two components, respectively. If we consider noble gases, the scattering lengths are all of the same order of magnitude. Therefore we do not have here the problem of widely different scattering strengths, in noble gases, as for the polarizabilities in the light scattering of noble gases. In particular the scattering length of Xe is 1.488 that of He.

An important point is that with neutron scattering, as was mentioned in Chapter 1, it is possible, in principle, to determine the $S_{ij}(k, \omega)$ separately .

In the next section I will present the results in dense He-Xe mixtures. The diameters of He and Xe are taken to be, following the method described in subsection 4.7.1, 2.21 Å and 3.91 Å, respectively. The mass of Xe in atomic units is 131.30, so that the mass ratio is about 33.

4.8 He-Xe mixtures

The results will be given in the BGK approximation $2M=16$ at most. We have learned, in the case of dilute mixtures, that, for the dynamic structure factors $S_{ij}(k, \omega)$, the results are quite insensitive to an increase in the number M already for $2M=10$. This is also true at high densities, when we compare the results from $2M=10$ and from $2M=16$. We recall that for dilute mixtures we found, in the BGK approximation with $2M=20$, two modes that propagate fast. However one of the two was not relevant for the dynamics. Here, with $2M$ at most equal to 16, we will always find only one fast mode, relevant for $S_{11}(k, \omega)$.

In the different subsections I will consider different densities n^* .

4.8.1 Density $n^*=0.4$

I plot in Fig. (4.15) 8 eigenvalues obtained in the BGK approximation $2M=10$ for the two relative concentrations $x_{\text{He}}=0.8$ and $x_{\text{He}}=0.6$. In Fig.

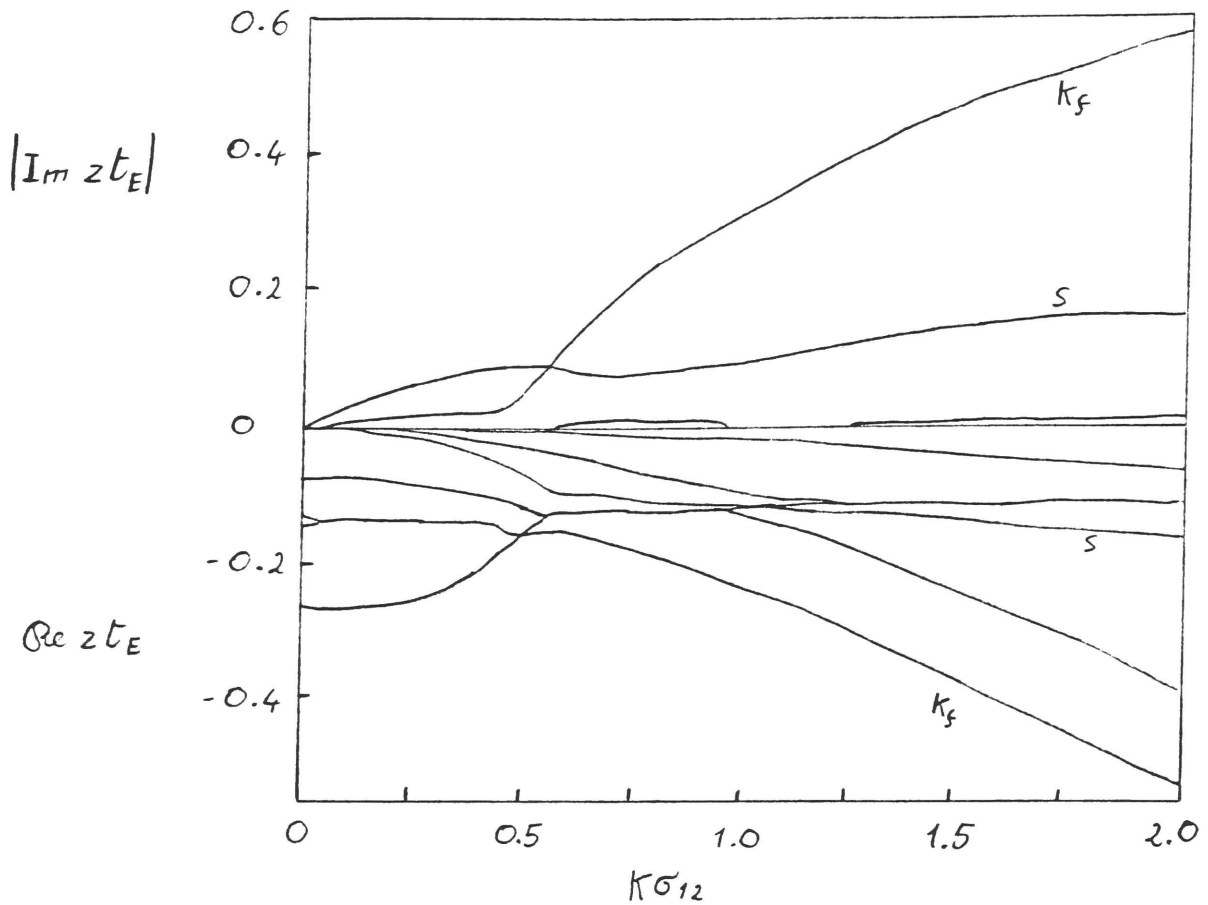


Fig. 4.15 a). 8 eigenvalues, in the BGK approximation with $2M=10$, for He-Xe with $n^*=0.4$ and $x_{He}=0.8$. With s and K_f I have indicated the eigenvalues associated with the extended sound mode and the fast propagating mode, respectively.

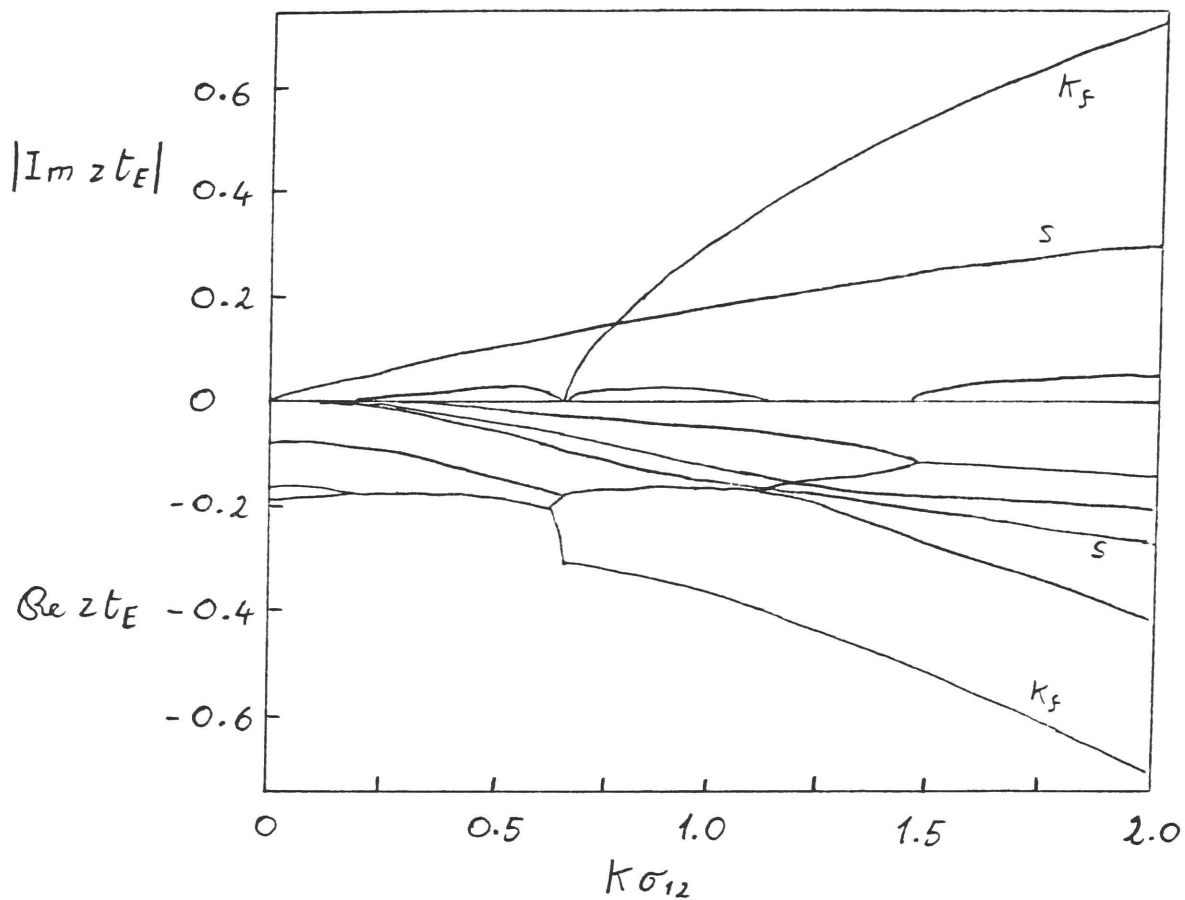


Fig. 4.15 b). 8 eigenvalues, in the BGK approximation with $2M=10$, for He-Xe with $\pi^*=0.4$ and $x_{He}=0.6$. s and κ_f like in a).

(4.16) I plot 11 eigenvalues obtained in the BGK approximation $2M=16$. The following features are similar to those obtained in dilute mixtures.

a) For both relative concentrations there is a kinetic fast propagating mode.

b) For $x_{\text{He}}=0.8$ the fast mode is a kinetic mode that begins to propagate for a rather small value of $k\sigma_{12}$, and then starts to propagate faster at a value of $k\sigma_{12}$ around 0.6, corresponding to values of $k\ell_1$ and $k\ell_2$ equal to 0.255 and 0.037 respectively. This happens both for the modes obtained for $2M=10$, Fig. (4.15), and those for $2M=16$, Fig. (4.16).

c) For $x_{\text{He}}=0.6$ the fast mode is a kinetic mode that begins to propagate fast immediately, for a value of $k\sigma_{12}$ around 0.65, corresponding to $k\ell_1=0.358$ and $k\ell_2=0.071$. Again, this happens for both BGK approximations.

d) The slope changes more rapidly than in dilute mixtures; however we can compute an average slope, in the graphs of Figs. (4.15) and (4.16), considering only the region where the mode is fast and the imaginary part of the eigenvalue of the fast mode is larger than that of the other modes. For both concentrations, the slope of the fast mode is very close to the velocity of sound in the pure fluid obtained removing the heavy Xe atoms.

e) The fast mode has always the largest damping, among all the plotted eigenvalues. But, like in dilute mixtures, is not so large to prevent a visible to $S_{11}(k, \omega)$ (see Fig. (4.17)).

f) The $S_{ij}(k, \omega)$ computed using matrix inversion are indistinguishable in the two approximations, $2M=10$ and $2M=16$, for both relative concentrations. Besides, the $S_{ij}(k, \omega)$ obtained using only the discrete eigenvalues plotted (8 and 11 respectively) are indistinguishable from those obtained by matrix inversion.

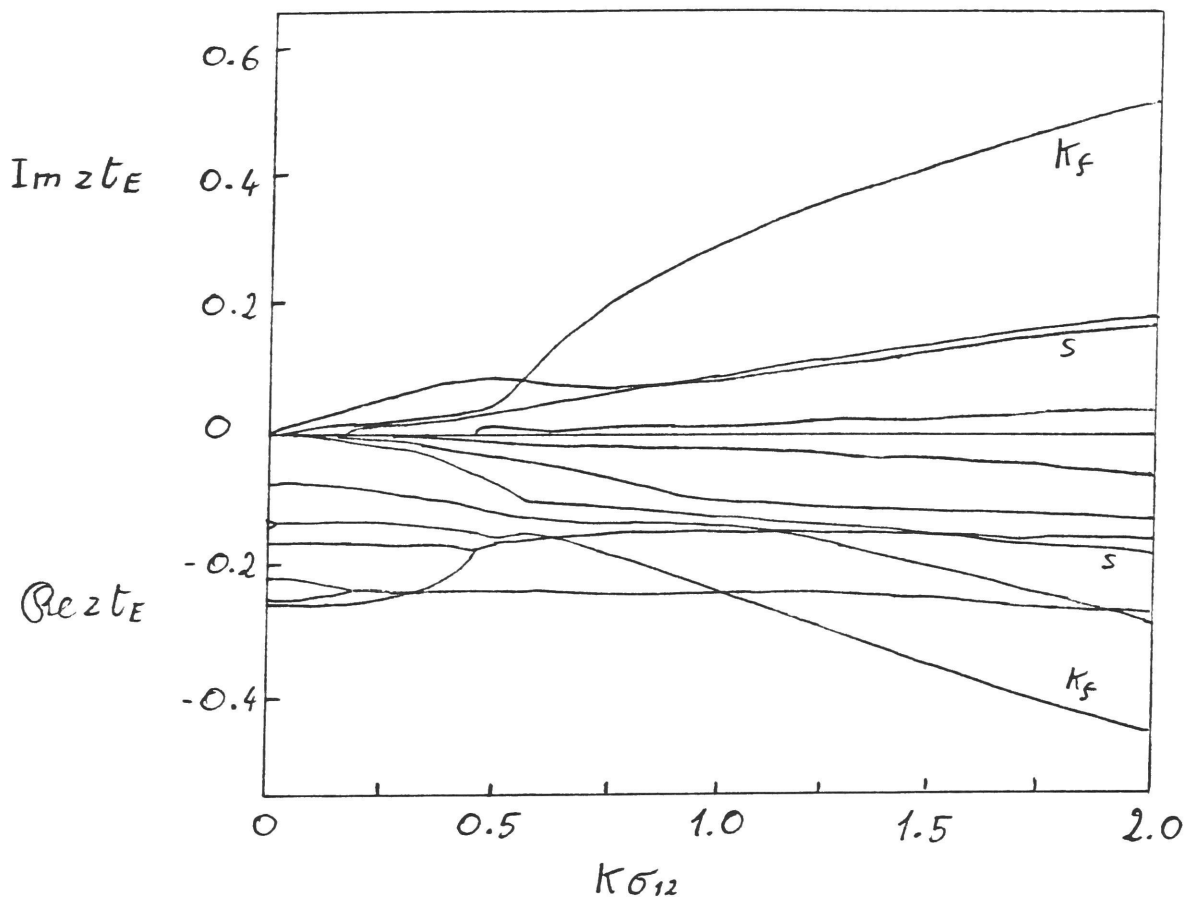


Fig. 4.16 a). 11 eigenvalues, in the BGK approximation with $2M=16$, for He-Xe with $n^*=0.4$ and $x_{He}=0.8$. s and k_f like in Fig. (4.15a).

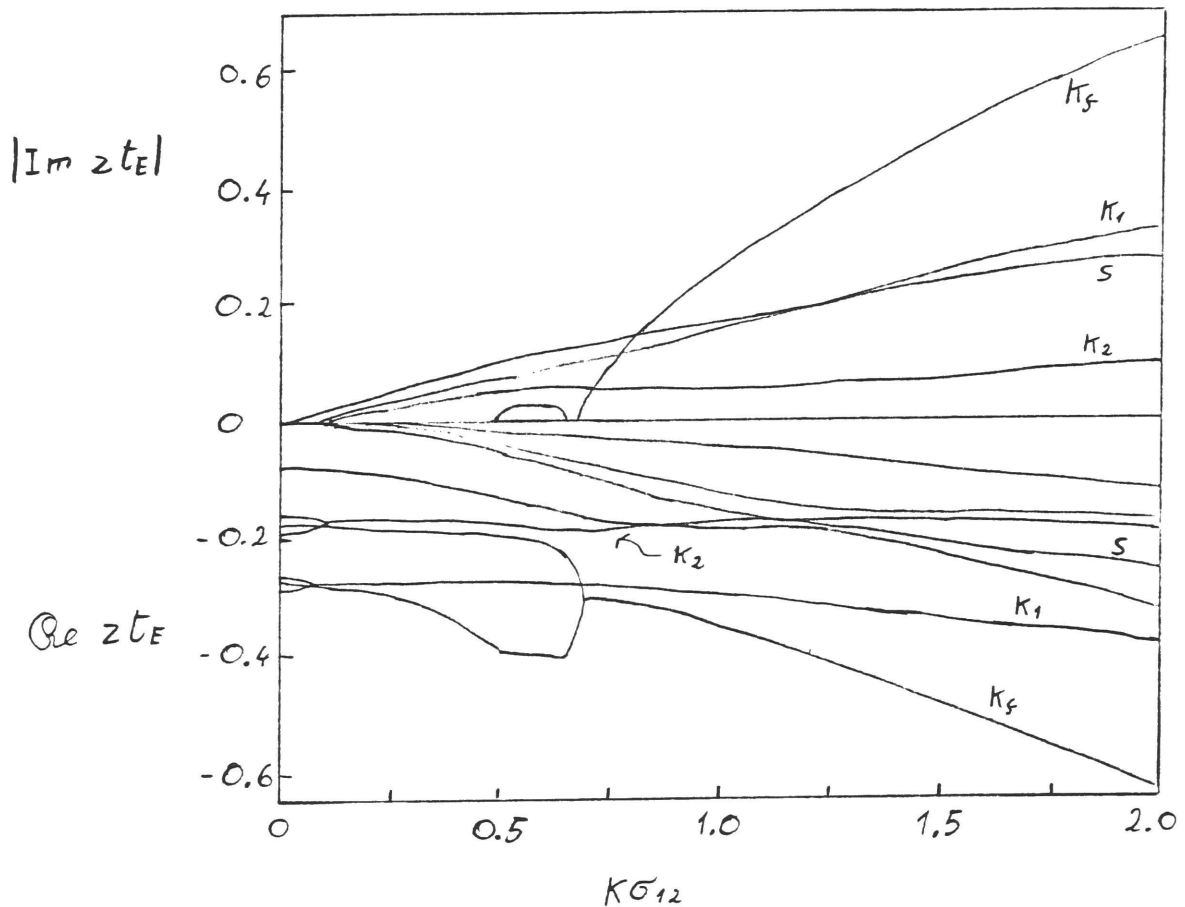


Fig. 4.16 b). 11 eigenvalues, in the BGK approximation with $2\pi=16$, for He-Xe with $n^*=0.4$ and $x_{He}=0.6$. I have indicated the eigenvalues corresponding to the propagating modes: s = extended sound mode; K_f = fast propagating mode; K_1 and K_2 = two other kinetic propagating modes.

In Fig. (4.17) I plot the $S_{ij}(k, \omega)$ and the differential scattering cross section $d^2\sigma/d\omega d\Omega$ for the relative concentration $x_{\text{He}}=0.6$ and $k\sigma_{12}=1.8$. We can clearly see the shoulder in $S_{11}(k, \omega)$. In the same figure I have also plotted $S_{11}(k, \omega)$ and $d^2\sigma/d\omega d\Omega$ obtained using the discrete eigenvalues, for $2M=16$, plotted in Fig. (4.16), except the fast mode. This does not affect $S_{12}(k, \omega)$ and $S_{22}(k, \omega)$, but it does affect $S_{11}(k, \omega)$.

However, there is the following difference with dilute mixtures. Although it is true that the fast mode contributes only to $S_{11}(k, \omega)$, we cannot say that the dynamics of the two components are "separate". In Table (4.3) I show the amplitudes of the contribution of the various modes to the $S_{ij}(k, \omega)$, and we see that there are eigenvalues, corresponding to propagating as well as non propagating modes, that have non negligible amplitudes in both $S_{11}(k, \omega)$ and $S_{22}(k, \omega)$, contrary to the dilute mixtures.

Now I consider other relative concentrations.

Like in dilute mixtures, if one increases the relative concentration of the light component, here He, the fast mode tends to disappear. First, it will be the extended sound mode that will have a jump in its slope and will propagate fast, until this jump disappears. I do not show the corresponding graphs, but also here we can take a value around 0.9 as the maximum relative concentration of He for the fast sound to occur.

Also similar to dilute mixtures is the behavior of dense mixtures when one decreases the relative concentration of He. The fast mode tends then to have an amplitude, in $S_{11}(k, \omega)$ (the only one of the $S_{ij}(k, \omega)$ where the amplitude is not negligible), with an imaginary part considerably larger than its real part, and this results in a broadening of the corresponding Lorentzian, causing a very slow decrease of $S_{11}(k, \omega)$, and not a shoulder.

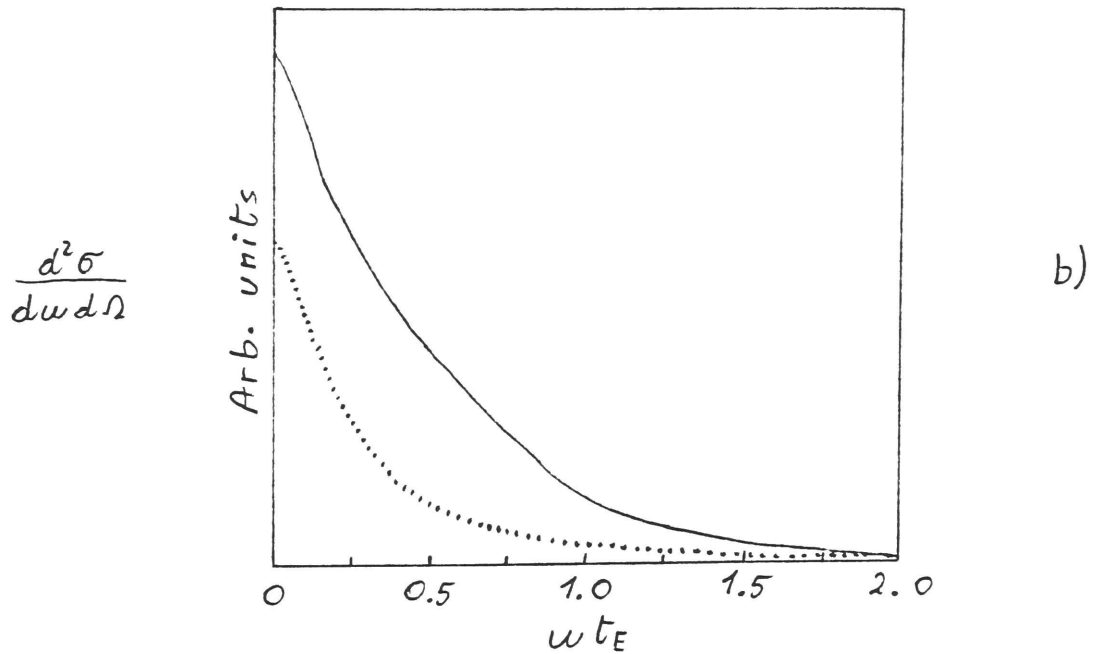
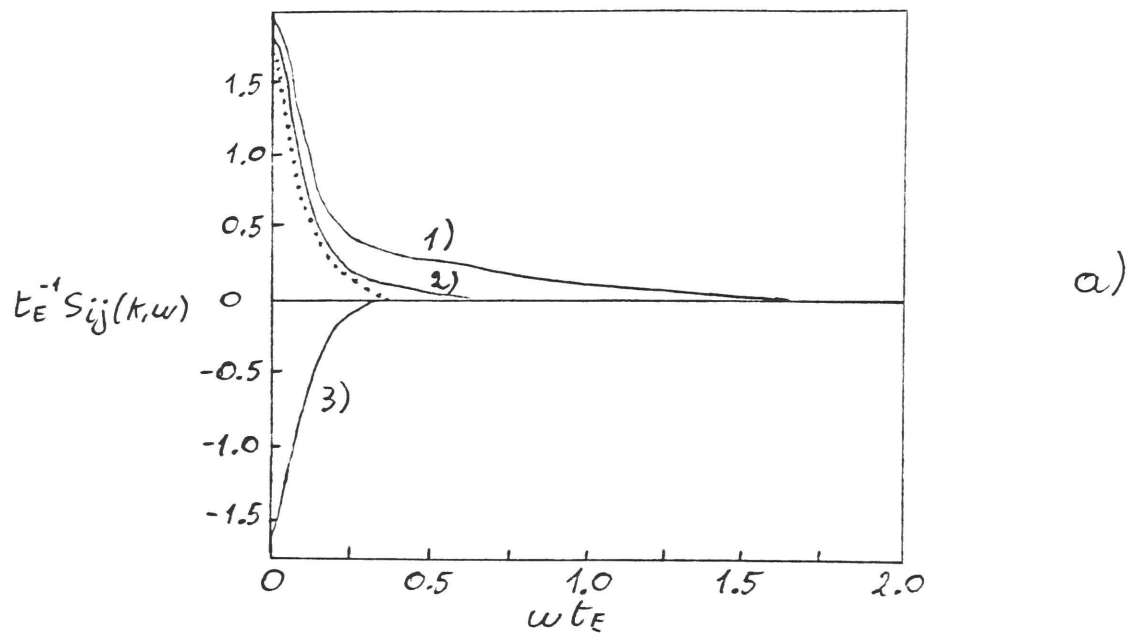


Fig. 4.17. a): $S_{ij}(k, \omega)$ for He-Xe with $n^* = 0.4$ and $X_{He} = 0.6$; the value of KG_{12} is 1.8. The curves 1), 2), and 3) correspond, respectively, to $S_{11}(k, \omega)$, $S_{22}(k, \omega)$, and $S_{12}(k, \omega)$; the dotted curve is $S_{11}(k, \omega)$ without the contribution of the fast mode. b): The differential scattering cross section; in the dotted curve the contribution of the fast mode is neglected.

TABLE 4.3

Amplitudes A_{ij} for the $S_{ij}(k, \omega)$, corresponding to the 11 eigenvalues of Fig. (4.16b), for $K\epsilon_2 = 1.8$. Here the eigenvalues associated with propagating modes are indicated with the same characters as in Fig. (4.16b).

Eigenvalue	A_{11}	A_{22}	A_{12}
-0.110	0.640	1.47	-0.940
-0.171	0.128	0.188	-0.155
$-0.243 + 0.257i$ s	$-0.035 - 0.007i$	$-0.029 - 0.047i$	$0.036 + 0.025i$
$-0.243 - 0.257i$ s	$-0.035 + 0.007i$	$-0.029 + 0.047i$	$0.036 - 0.025i$
-0.282	0.273	2×10^{-5}	0.002
$-0.189 + 0.079i$ K_2	$-0.215 - 0.088i$	$-0.298 - 0.273i$	$0.258 + 0.164i$
$-0.189 - 0.079i$ K_2	$-0.215 + 0.088i$	$-0.298 + 0.273i$	$0.258 - 0.164i$
$-0.371 + 0.295i$ K_1	$0.001 + 6 \times 10^{-4}i$	$5 \times 10^{-4} + 0.001i$	$-9 \times 10^{-4} - 0.001i$
$-0.371 - 0.295i$ K_1	$0.001 - 6 \times 10^{-4}i$	$5 \times 10^{-4} - 0.001i$	$-9 \times 10^{-4} + 0.001i$
$-0.575 + 0.585i$ K_f	$0.220 - 0.253i$	$4 \times 10^{-4} + 3 \times 10^{-5}i$	$-0.005 - 0.011i$
$-0.575 - 0.585i$ K_f	$0.220 + 0.253i$	$4 \times 10^{-4} - 3 \times 10^{-5}i$	$-0.005 + 0.011i$

For dense mixtures I found that this happens for relative concentrations somewhat lower than for dilute mixtures, at about a value $x_{\text{He}}=0.3$, so that this is the lower limit of the He concentration, for which fast sound can be observed in dense mixtures.

To complete the analysis, I show in Fig. (4.18) the 8 effective eigenvalues obtained starting with $2M=16$, for the relative concentration $x_{\text{He}}=0.8$. The $S_{ij}(k, \omega)$ computed using these 8 eigenvalues are indistinguishable from those obtained by matrix inversion.

4.8.2 Higher densities

In Fig. (4.19) we see 11 eigenvalues, from the BGK approximation with $2M=16$, for the density $n^*=0.6$ and relative concentrations $x_{\text{He}}=0.8$ and $x_{\text{He}}=0.6$ respectively. Now we see that for $x_{\text{He}}=0.8$ it is the extended sound mode that becomes fast propagating, while for $x_{\text{He}}=0.6$ it is a kinetic mode. In Fig. (4.20) I plot the 11 eigenvalues for the density $n^*=0.8$ and relative concentrations $x_{\text{He}}=0.6$ and $x_{\text{He}}=0.5$, respectively. We see that we do not have a fast propagating mode any more. In order to have a hint on why this happens we can use the result that we have always found: when there is a fast mode, its group velocity is close to the sound velocity of the pure fluid obtained by removing the heavy atoms. In a dense He-Xe mixture with $n^*=0.8$ the following happens: the mixture is so dense that the velocity of sound is very high; when we remove the heavy atoms, although we could expect a higher velocity of sound because now we have only light atoms, the decrease in density is such that actually the velocity of sound is lower. This does not happen in dilute mixtures because at low density the velocity

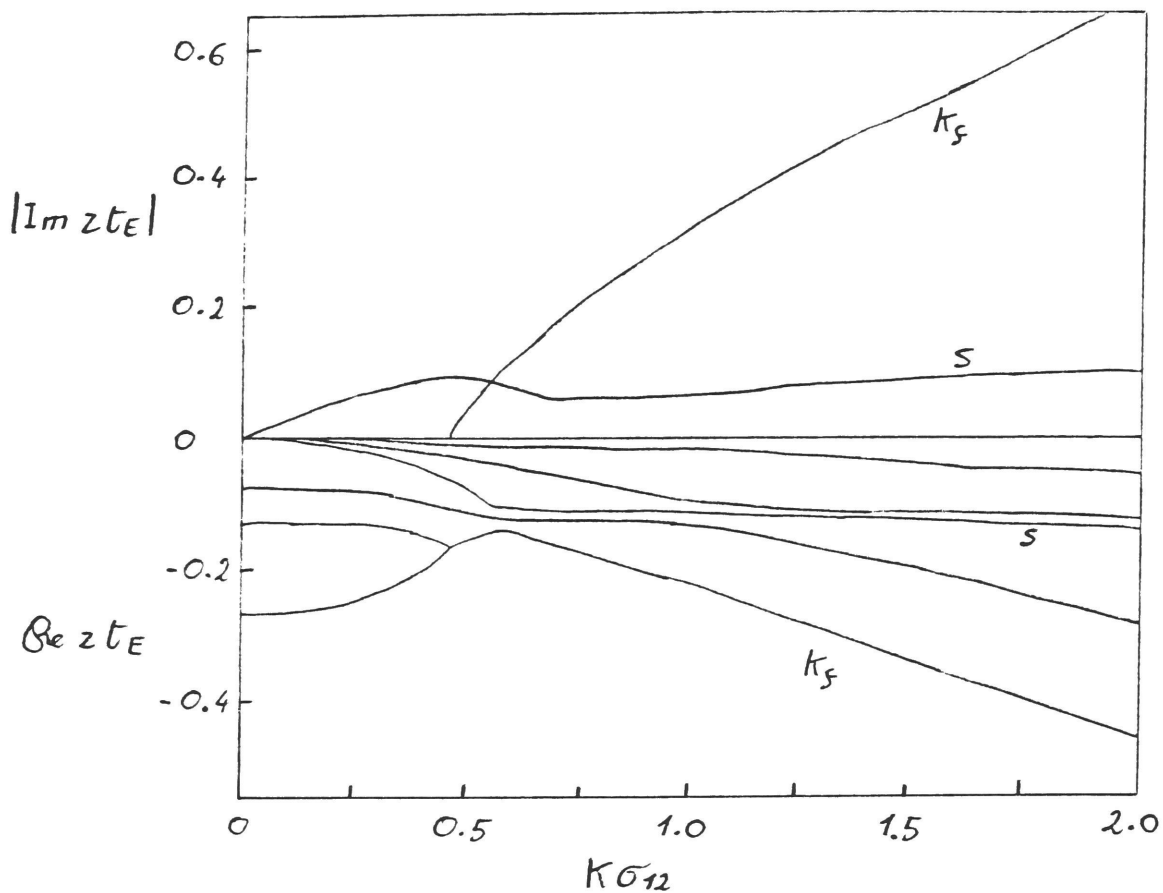


Fig. 4.18. 8 effective eigenvalues in He-Xe with $\pi^* = 0.4$ and $X_{He} = 0.8$. s and k_s like in Fig. (4.15a).

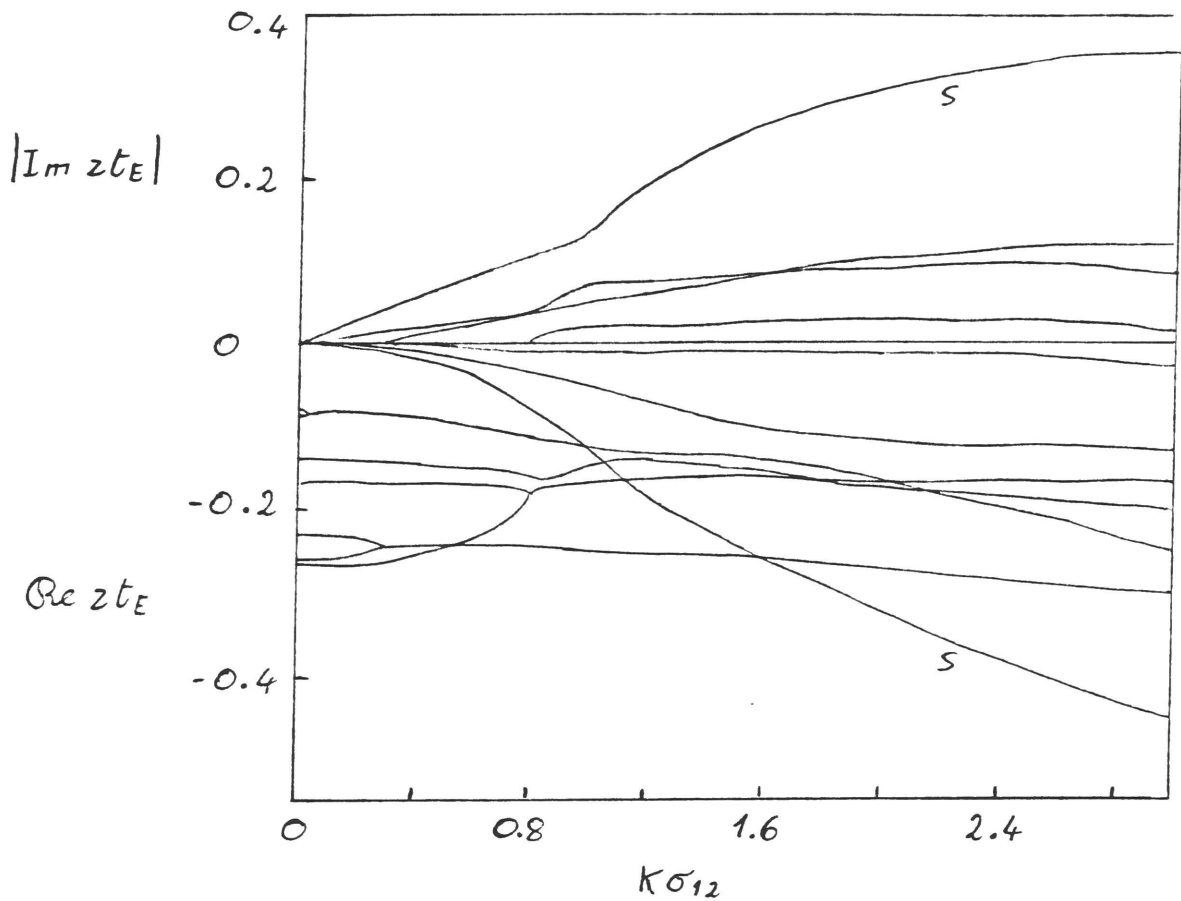


Fig. 4.19 a). 11 eigenvalues, in the BGK approximation with $2N=16$, for He-Xe with $\pi^*=0.6$ and $x_{He}=0.8$. It is the extended sound mode (the corresponding eigenvalue is indicated by s) that becomes fast propagating.

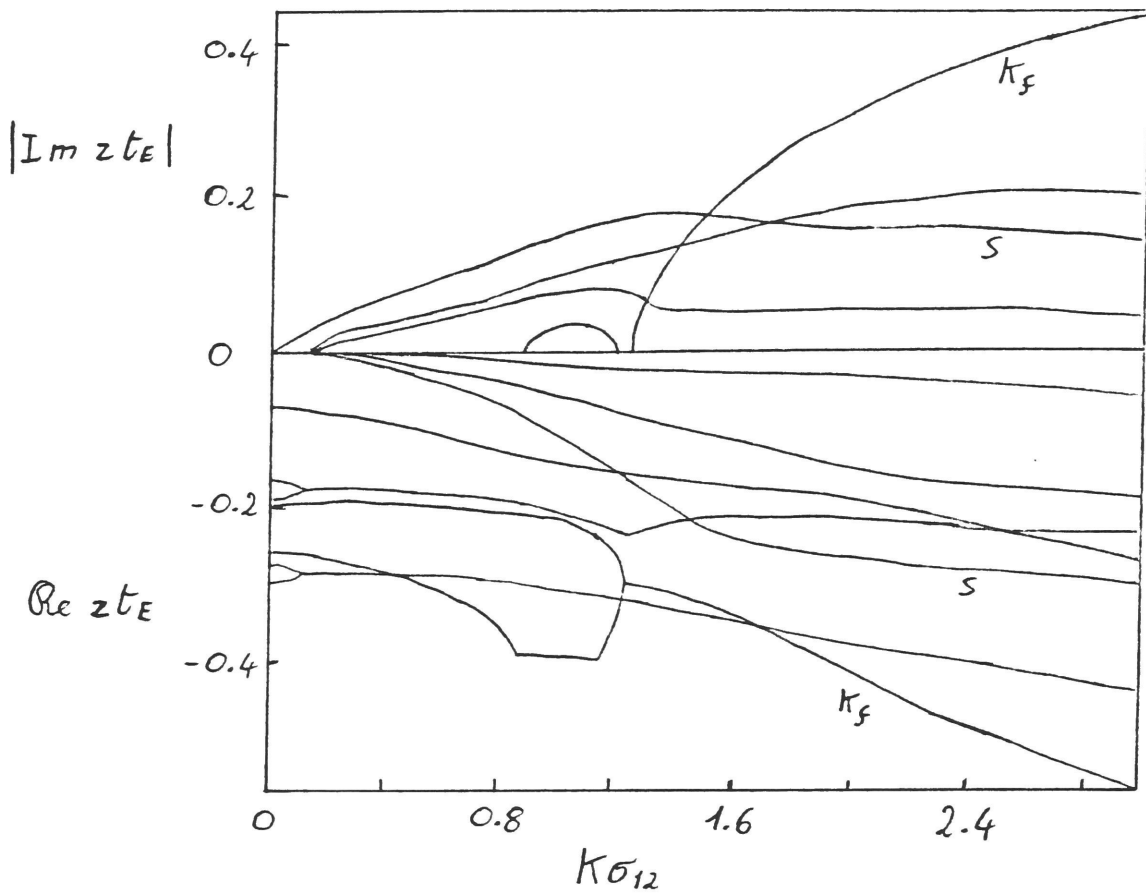


Fig. 4.19 b). 11 eigenvalues, in the B6K approximation with $2M=16$, for He-Xe with $\eta^*=0.6$ and $X_{He}=0.6$. s and κ_f indicate the eigenvalues associated with the extended sound mode and the fast propagating mode, respectively.

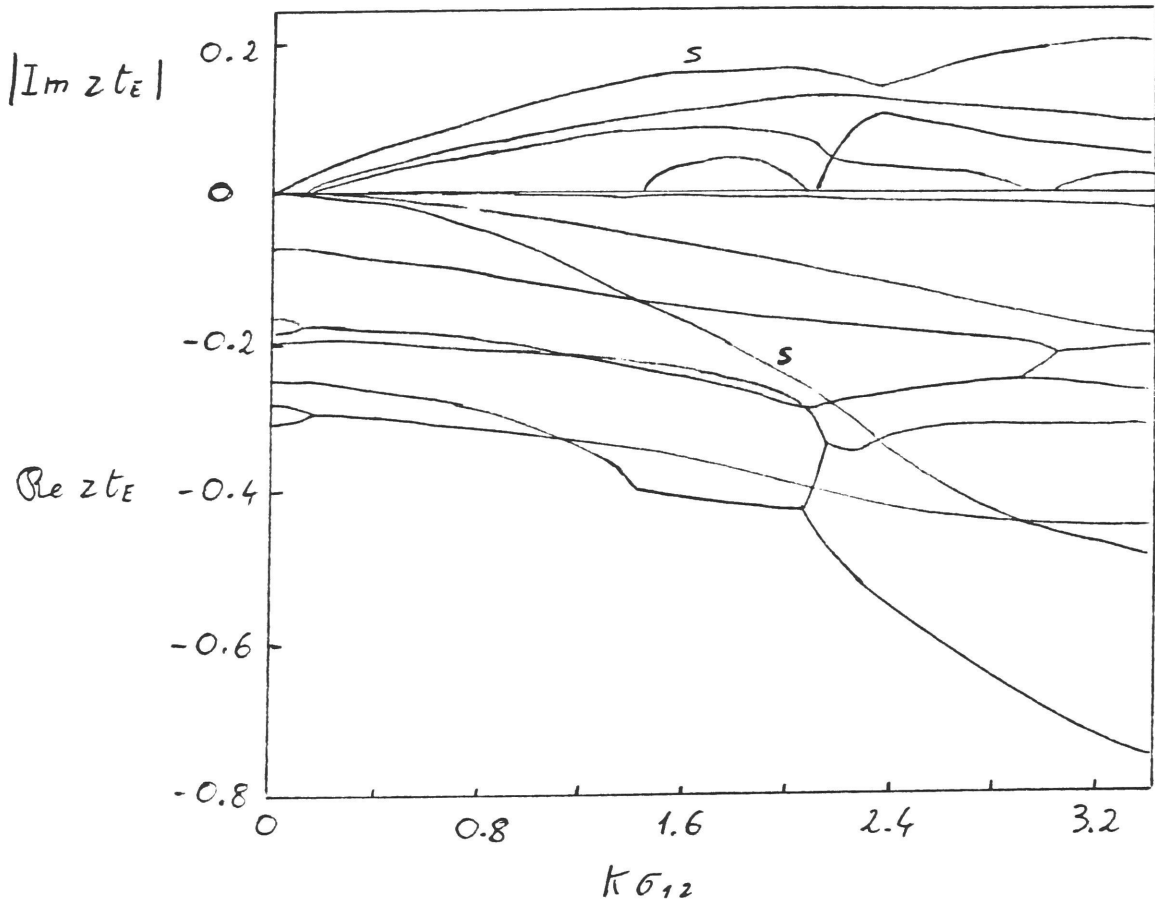


Fig. 4.20 a). 11 eigenvalues, in the BGK approximation with $2M=16$, for He-Xe with $n^*=0.8$ and $X_{He}=0.6$. s indicates the eigenvalue associated with the extended sound mode.

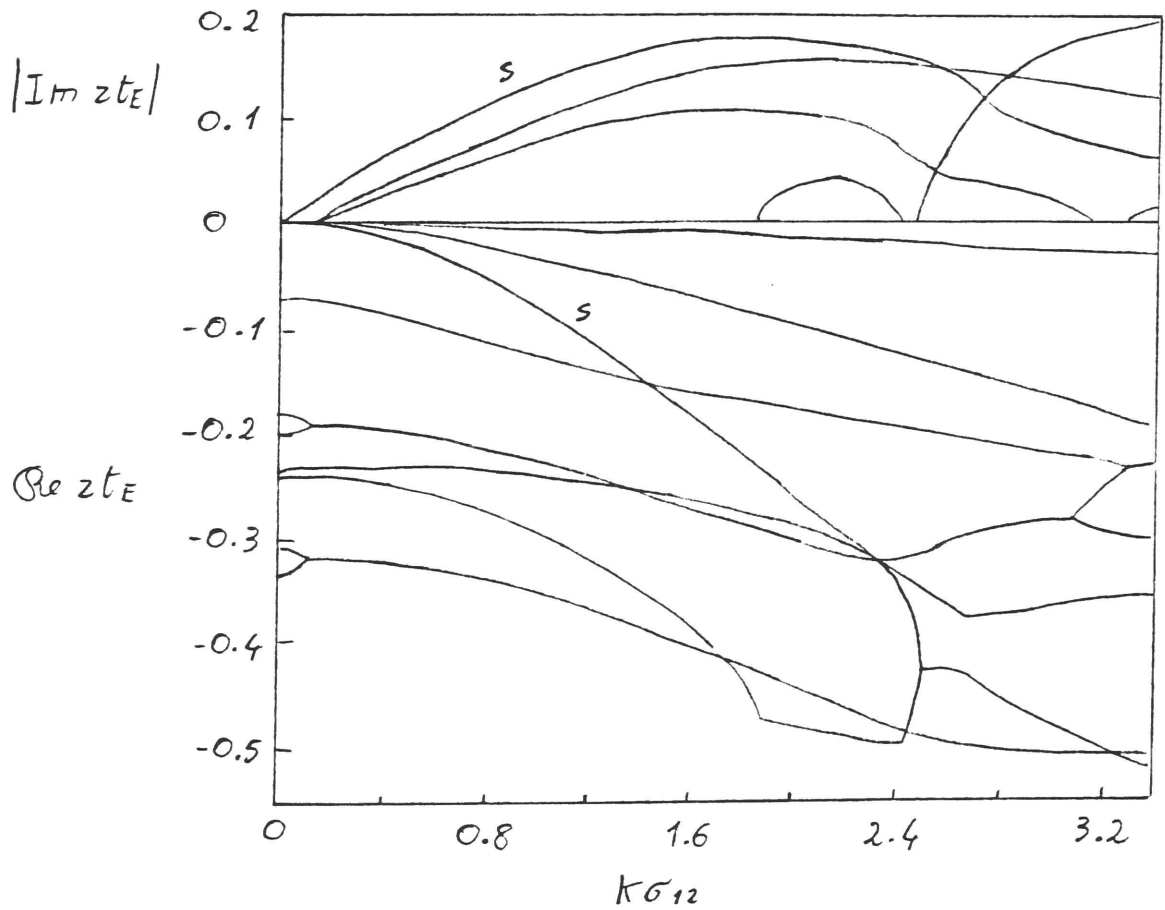


Fig. 4.20 b). 11 eigenvalues, in the BGK approximation with $2M=16$, for He-Xe with $n^*=0.8$ and $X_{He}=0.5$. s like in a).

of sound of a given fluid (simple fluid or binary mixture) is quite independent of the density. Therefore we can argue that the reason for the disappearance, at very high density, of the fast mode, is that there is no velocity of propagation, higher than the velocity of sound in the mixture, at the "disposition" of the fluid.

Using this interpretation, i. e., that a mixture "tries" to have a mode of propagation with the velocity of propagation close to the velocity of sound of the pure fluid of the light particles, we can make the following comment on the result that, at the higher relative concentrations (at densities lower than $n^*=0.8$), it is the extended sound that becomes the fast mode, and not a kinetic mode: at higher concentrations the difference between the velocity of sound of the mixture and that of the pure fluid of the light component is small, and therefore the extended sound mode has to make only a small change in slope to become a fast mode. This seems to be preferred to the appearance of a fast kinetic mode. Instead, when the difference between the two velocities is large and the extended sound should make a large jump, then it seems preferred to have a kinetic fast mode. However, I should add that, outside the hydrodynamic regime, there is no strong reason to give a special meaning to the extended sound mode, simply because of its behavior for $k \rightarrow 0$, when it is the only propagating mode, the hydrodynamic (ordinary) sound, in the fluid.

I can call the cause of the disappearance of the fast mode at high density a size effect. For, the heavier atoms are also the larger ones, and if we remove them the density n^* (now equal to $n_1 \sigma_1^3$ instead of $n_1 \sigma_1^3 + n_2 \sigma_2^3$) becomes much smaller. A nice illustration of this is the following. I have computed the eigenvalues, in the BGK approximation with $2M=10$, for the

density $n^*=0.8$ and the relative concentration $x_{\text{He}}=0.8$. Then I have computed the analogous eigenvalues putting artificially the diameter of Xe equal to that of He; this resembles the conditions of the computer experiment by Bosse et al., mentioned in section 4.7, because they used the same length for both atoms (Li and Pb) to characterize the short range repulsion. The two sets of eigenvalues are plotted in Fig. (4.21). We see that in the case of equal diameters the fast mode exists, and that its initial slope is actually about 40% higher than the velocity of sound of the pure He fluid obtained by removing the Xe atom. This suggests that, if our diameters were equal, the trend of the fast mode would have been the following: increasing the density, its velocity of propagation would increase more than the velocity of sound of the pure fluid of the light particles. However, if we compute the $S_{ij}(k, \omega)$ in this case of equal diameters and $n^*=0.8$, $x_{\text{He}}=0.8$, we do not find a visible shoulder in $S_{11}(k, \omega)$ (I do not show the graphs). This is contrary to what was found by Bosse et al.: they had even a peak. The reason could reside in the larger damping in our hard sphere mixture.

4.9 Other mixtures

I briefly consider here two other mixtures, He-Kr and He-Ar. In atomic units the mass of Kr is 83.80, so that the mass ratio in He-Kr is about 21, while the mass ratio in He-Ar is about 10 (we recall that in atomic units the masses of He and Ar are 4.003 and 39.44 respectively). The diameters of Ar and Kr (at high densities), are 3.276 Å and 3.536 Å respectively.

An example is given in Fig. (4.22): both mixtures for $n^*=0.4$ and $x_{\text{He}}=0.6$. We have a fast propagating mode in He-Kr, but not in He-Ar. In

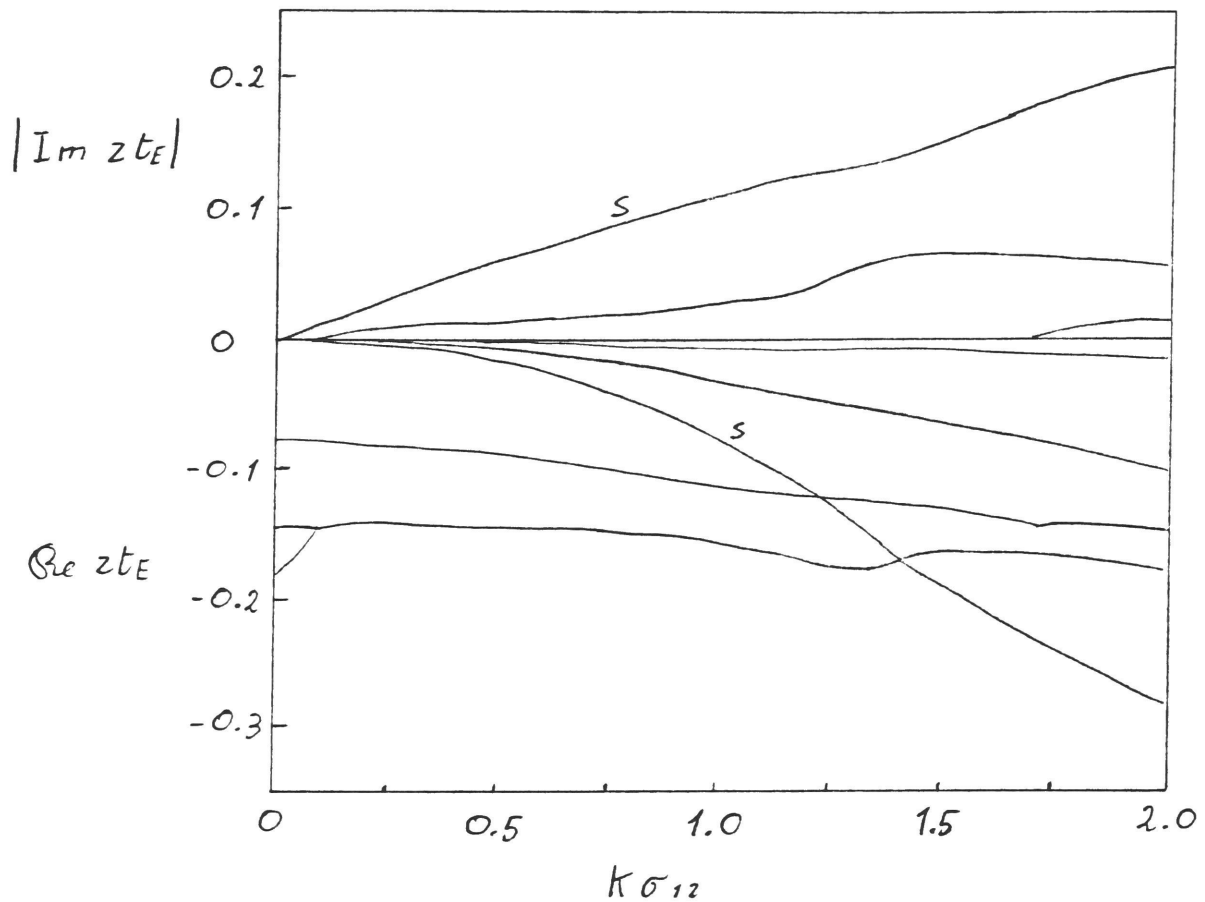


Fig. 4.21 a). 8 eigenvalues, in the BGK approximation with $2M=10$, for He-Xe with $n^*=0.8$ and $X_{He}=0.8$. s like in Fig. (4.20a).

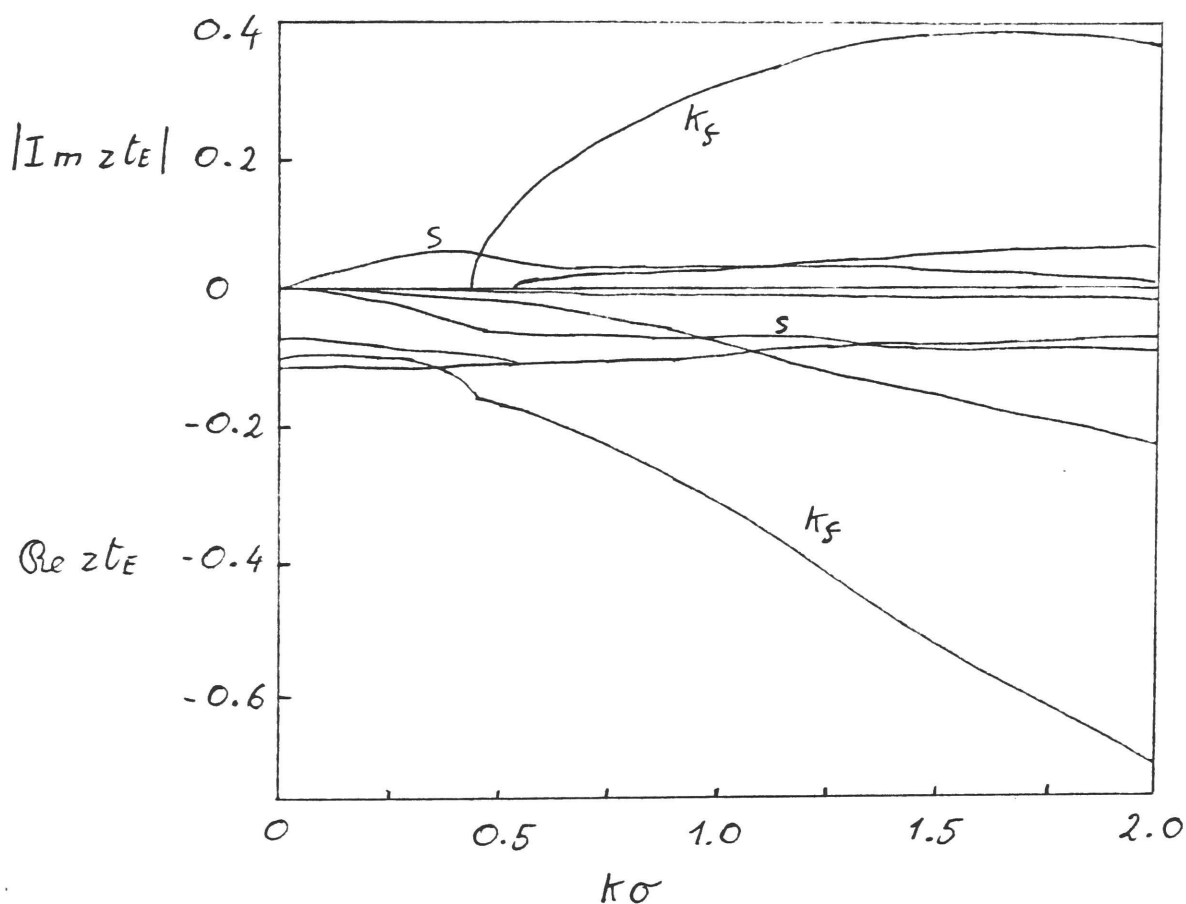


Fig. 4.21 b). 8 eigenvalues, in the BGK approximation with $2M=10$, for He-Xe with $n^*=0.8$ and $x_{\text{He}}=0.8$. Here the two diameters are equal: $\sigma_{\text{He}}=\sigma_{\text{Xe}}=\sigma$. The eigenvalue associated with the fast propagating mode is denoted by k_f ; s like in Fig. (4.20a).

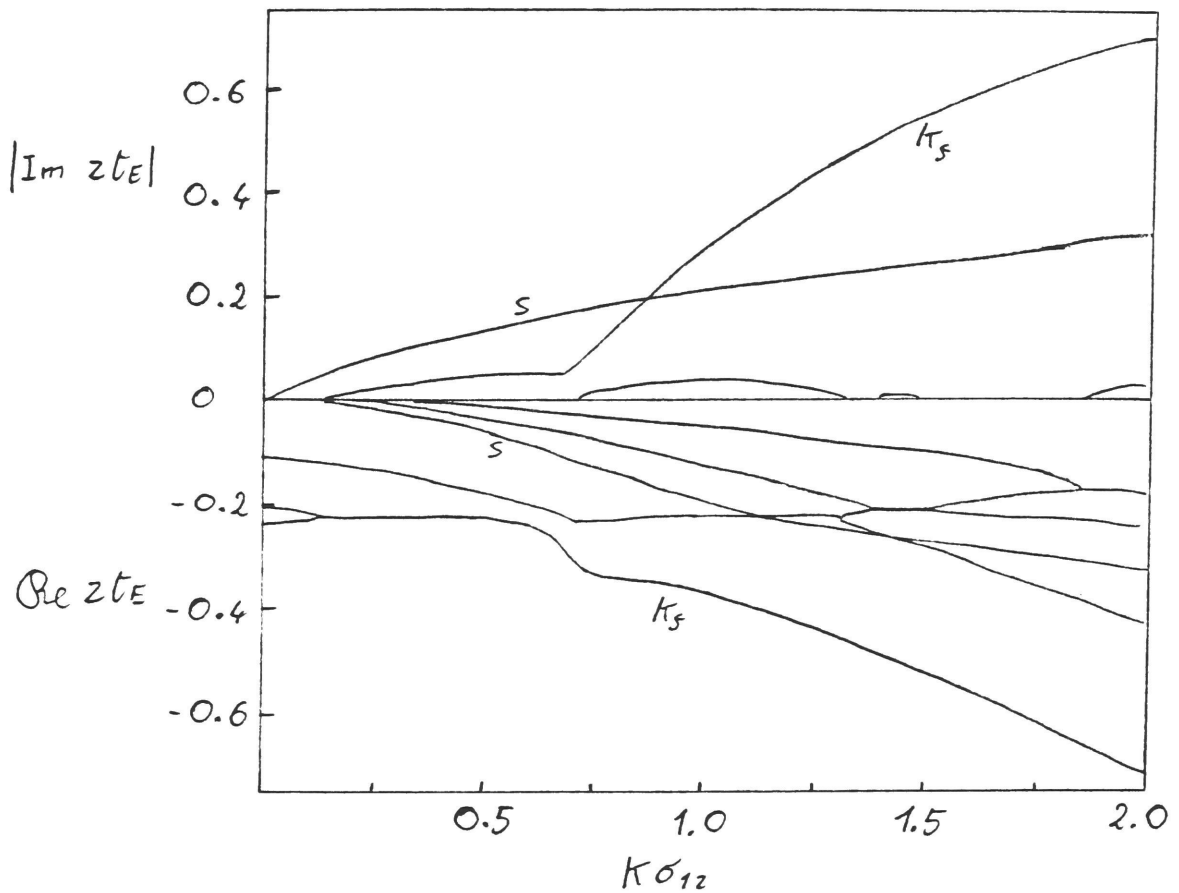


Fig. 4.22 a). 8 eigenvalues, in the BGK approximation with $2n=10$, for He-Kr with $n^*=0.4$ and $x_{\text{He}}=0.6$. s and κ_s like in Fig. (4.15a).

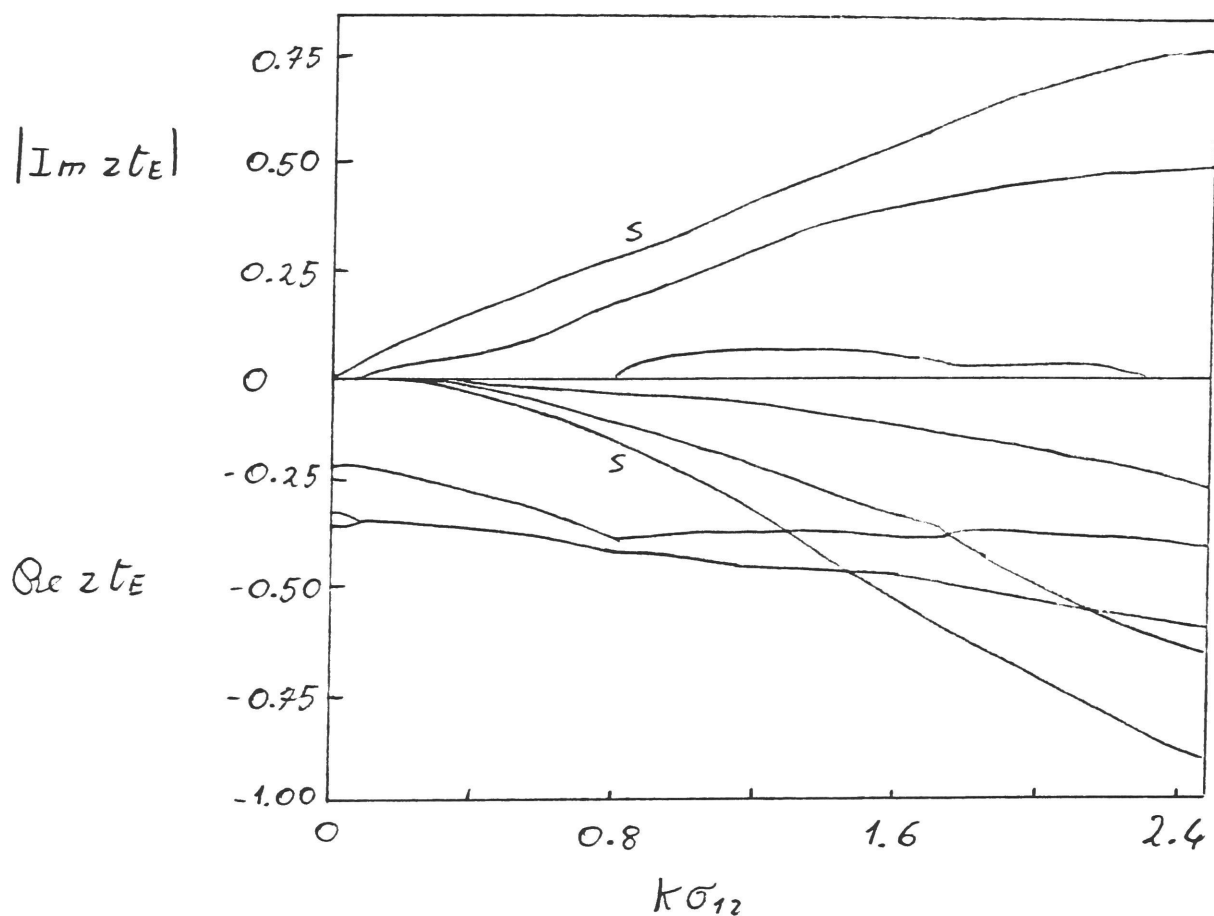


Fig. 4.22 b). 8 eigenvalues, in the BGK approximation with $2M=10$, for He-Ar with $\pi^*=0.4$ and $X_{He}=0.6$. s like in Fig. (4.20 a).

dilute mixtures we found a fast mode (in a H_2 -Ne mixture) for about the same mass ratio as in He-Ar. This seems to suggest that increasing the density a larger mass ratio is necessary, in order to have fast sound. However, this point has not been investigated further.

Notes

[1] Actually, because of the singular nature of the potential, for hard sphere fluids, both simple fluid and mixtures, the temperature scales out. It is only necessary to determine the average kinetic energy and the mean free time between collisions (see below in the text). For a simple hard sphere fluid the only relevant parameter is the reduced density $n\sigma^3$.

[2] The different physical situation between forced sound propagation and propagation of spontaneous fluctuations must be stressed. In the first case a small external perturbation causes a macroscopic disturbance in one point of the fluid with a given frequency ω , and this disturbance propagates, while it is dissipated, through the fluid. In typical experiments one measures the velocity of propagation of the disturbance and its attenuation. The difference from the process of decay of spontaneous microscopic fluctuations is then clear, since no external disturbing frequency is involved here.

[3] In disparate-mass binary mixtures in general ℓ_2 is several times smaller than ℓ_1 , where with 1 I have indicated the light component. If we look at (4.2) and (4.3) we realize this by noting the following: m_2/m_1 is a number large compared to 1; besides σ_2 is larger than σ_1 (the heavier component has

also a larger diameter), so that we easily see from (3.25) that, for given values of n_1 and n_2 , also the inequalities $\chi_{11} < \chi_{12} < \chi_{22}$ are satisfied. Therefore it turns out that ℓ_2 is several times smaller than ℓ_1 .

[4] This phenomenon will be found also for high densities. However, it must be noticed that, as long as we consider low density fluids, the density of the fluid is not an important quantity for the velocity of sound, since at low densities the velocity of sound is practically independent of the density. Therefore, I could have simply said that the group velocity of the fast mode is very close to the velocity of sound of a (low density) pure H_2 fluid. However, at high densities I found that the pure light component fluid, for which the velocity of sound is close to the group velocity of the fast mode in the mixture, is the fluid obtained by removing all the heavy particles. Therefore I kept the same expression here, for low densities.

[5] In general this "equivalent" hard sphere diameter for high density hard sphere fluids will depend on the temperature, although not very strongly.

Conclusions

5.1 Discussion

The main subject of this thesis has been the study of the characteristic behavior of disparate-mass binary fluid mixtures. When, in this class of fluids, we explore what happens outside the hydrodynamic regime, we find a new phenomenon: one of the decay modes of the density fluctuations is a very fast propagating mode involving only the light particles. This implies a sort of "separation" of the dynamics of the light from that of the heavy particles. About this result I make the following remarks.

a) As explained in Chapter 1, the correlation functions of the density fluctuations are directly observable in light and neutron scattering experiments. We have seen that the presence of this fast propagating mode can be detected in such experiments. In fact I found that the fast propagating mode causes a shoulder in $S_{11}(k, \omega)$ as well as in $d^2\sigma/d\omega d\Omega$, the differential scattering cross section. Of course the analysis of experimental data has a disadvantage with respect to that of our theoretical results: to disentangle the contributions of the different $S_{ij}(k, \omega)$ from the observed differential scattering cross section is not an easy task. I have noted that this could be approximately achieved, in light scattering experiments, only on the basis of plausibility arguments, given in section 4.5, since there is no way to separate, from the total differential

scattering cross section, the three terms corresponding to the different $S_{ij}(k, \omega)$. The situation is different in neutron scattering, where a variation of the isotopic composition of the mixture allows the experimentalist to extract, in principle, the different $S_{ij}(k, \omega)$.

b) One can argue that the presence of the fast mode, propagating only through the light particles, can be explained by saying that it involves a frequency too high for the heavy particles to follow. However, it is not clear what the detailed physical mechanism is that gives rise to the fast mode, and in particular it is not clear why the overall picture, at least concerning the fast mode, is very similar for dilute and dense mixtures.

c) It is worthwhile to note that the mass ratio need not be very large, in order to have an observable fast mode in dilute mixtures. On the other hand, in dense mixtures I found that, for a mass ratio of about 10, like in He-Ar, there is no fast mode. Concerning this last point, see also the next section, in point a).

d) Another important feature is the stability I found of the $S_{ij}(k, \omega)$ with respect to the change of the number M , that determines the order of the BGK approximation in our kinetic theory. This means that for a not very large value of M , the corresponding approximate kinetic operator selects all the relevant modes that are necessary to describe the dynamics of the density fluctuations.

e) Although the modes change with M in a complicated way it is important to observe that the fast mode, not only is always present, but also does not change appreciably its most important characteristics, like the range in k where it appears, and its slope, that gives its velocity of propagation.

5.2 Open questions

There are a number of problems that deserve further attention.

a) A very important point is a possible detailed comparison with experiments, when they will provide results on the k regions relevant for the predictions presented in this thesis. The experimental results would be important on two grounds. First, if they confirm, at least qualitatively, what has been found theoretically, it would be the first time in which a non hydrodynamic mode is clearly "seen" through the spectrum of the density fluctuations. Second, on more general grounds, they would provide information on the extent of the validity of the hard sphere approximation for real binary mixtures. It could happen, for example, that in real mixtures the damping of the fast mode is smaller than in hard sphere mixtures, causing the possibility to have a peak, rather than a shoulder, in $S_{11}(k, \omega)$; and an observable effect could also be visible in not so disparate-mass dense mixtures. Actually, in a very recent preprint²¹⁾ (March 1989), concerning neutron scattering experiments in dense He-Ne mixtures, fast sound has been reported.

b) Since a fast mode has been found both for dilute and dense mixtures, one could wonder whether such a mode would not exist in disparate-mass solid mixtures. One would then have fast phonons propagating exclusively in the light component with a velocity greater than the velocity of sound of the solid mixture. A preliminary model calculation of a damped phonon propagation in solid mixtures would indicate that the above conjecture has some ground. However, the model is very crude, and therefore at present it is not possible to draw any conclusion.

c) As was pointed out, in note [2] of Chapter 4, the physical situation of forced sound propagation in fluids is different from that of microscopic density fluctuations. However, the modes in the two cases come from the same dispersion relation $F(k, \omega) = 0$, obtained by looking for plane wave solutions of the hydrodynamic or kinetic equations: for forced sound propagation one solves for k in terms of a real ω , while for the study of fluctuations one solves for ω in terms of a real k . Therefore a closer study of the connection between these two sets of modes would be interesting.

d) Also a more complete discussion of the behavior of the various eigenvalues would be interesting. For example, looking at Fig. (4.2), we see that the slowest propagating mode has a propagation gap. Propagation gaps have been found also in simple hard sphere fluids⁵⁾. One could then investigate this phenomenon in binary mixtures.

Appendix I

Here I prove the expression (2.63). From (2.53) it follows that:

$$\bar{F}_{\ell m}^E(k, t) = \frac{1}{2\pi i} \int_{s-i\infty}^{s+i\infty} dz e^{zt} \tilde{S}_{\ell m}^E(k, z) \quad (\text{AI.1})$$

where the real number s is larger than the real part of any singularity of $\tilde{S}_{\ell m}^E(k, z)$. If the number of these singularities, for $\text{Re } z$ finite, is finite, we can deform the path of integration, sending $s \rightarrow -\infty$, provided that we have "appendices" from this path that encircle the singularities. Therefore, from the theorem of residues, we have:

$$\bar{F}_{\ell m}^E(k, t) = \sum_n \text{Res} \left(e^{zt} \tilde{S}_{\ell m}^E(k, z) \right) + \bar{F}_{\ell m}^E \text{ess}(k, t) \quad (\text{AI.2})$$

Here the sum runs over the singularities of $\tilde{S}_{\ell m}^E(k, z)$, and

$$\bar{F}_{\ell m}^E \text{ess}(k, t) = \lim_{s \rightarrow -\infty} \frac{1}{2\pi i} \int_{s-i\infty}^{s+i\infty} dz e^{zt} \tilde{S}_{\ell m}^E(k, z) \quad (\text{AI.3})$$

is the contribution from the essential singularity for $\text{Re } z = -\infty$. We write:

$$\left(I - A(k, z)H(k) \right)^{-1} = \frac{1}{D(k, z)} G(k, z) \quad (\text{AI.4})$$

with the matrices $A(k, z)$, $H(k)$, $G(k, z)$, and the number $D(k, z)$ defined in section 2.2. The poles of $\frac{1}{D(k, z)} [G(k, z)A(k, z)]_{\ell m}$ in (2.60) are the values of z for which $D(k, z) = 0$. We denote these values with $z_n(k)$. Neglecting the second term in (AI.2), we have, from the rule for computing the residues, that:

$$\begin{aligned} \bar{F}_{\ell m}^E(k, t) &= \sum_n \text{Res} \left(e^{zt} \tilde{S}_{\ell m}^E(k, z) \right) = \\ &= \sum_n \text{Res} \left(e^{zt} \frac{1}{D(k, z)} [G(k, z)A(k, z)]_{\ell m} \right) = \sum_n \frac{e^{z_n(k)t}}{D'(k, z_n(k))} [G(k, z_n(k))A(k, z_n(k))] = \end{aligned}$$

$$= \sum_n M_{\ell m, n}(k) e^{z_n(k)t} \quad (\text{AI.5})$$

where the definitions (2.64) and (2.65) have been used. The Laplace transform of this expression is:

$$\sum_n \frac{M_{\ell m, n}(k)}{z - z_n(k)} \quad (\text{AI.6})$$

which is expression (2.63).

Appendix II

In this appendix I explain how the effective modes are defined and how the correlation functions are computed using the effective modes. For simplicity, I will restrict myself to simple fluids.

I start from the expression (2.52), that gives the correlation functions in the simple fluid kinetic theory:

$$\bar{F}_{\ell m}^E(k, t) = \langle \psi_{\ell}(\vec{v}_1), e^{tL_E(\vec{k})} \psi_m(\vec{v}_1) \rangle_1 \quad (\text{AII.1})$$

Since the ψ 's are a complete set of functions, it follows from (AII.1) that:

$$\frac{d}{dt} \bar{F}_{\ell m}^E(k, t) = \sum_{n=1}^{\infty} L_{\ell n}^E(k) \bar{F}_{nm}^E(k, t) \quad (\text{AII.2})$$

where with $L_{\ell m}^E(k)$ I have indicated the matrix elements of the kinetic operator $L^E(\vec{k})$. The Laplace transform of (AII.2) gives:

$$z \tilde{S}_{\ell m}^E(k, z) = \sum_{n=1}^{\infty} L_{\ell n}^E(k) \tilde{S}_{nm}^E(k, z) + \delta_{\ell m} \quad (\text{AII.3})$$

where $\tilde{S}_{\ell m}^E(k, z)$ is defined by (2.53) and use has been made of the orthonormality relation (2.6). From (AII.3) one can obtain M' effective modes using the following procedure. First, we consider a given value of m in (AII.3) such that $m \leq M'$. Then the functions $\tilde{S}_{nm}^E(k, z)$ with $n > M'$ can be eliminated in the M' equations (AII.3) with $\ell \leq M'$, solving successively the equations for $\tilde{S}_{nm}^E(k, z)$ with $n > M'$ in terms of the $\tilde{S}_{nm}^E(k, z)$ with $n \leq M'$. Then one obtains an $M' \times M'$ matrix equation for the $\tilde{S}_{\ell m}^E(k, z)$ with $\ell, m \leq M'$:

$$z \tilde{S}_{\ell m}^E(k, z) = \sum_{n=1}^{M'} W_{\ell n}(k, z) \tilde{S}_{nm}^E(k, z) + \delta_{\ell m} \quad (\text{AII.4})$$

with:

$$W_{\ell m}(k, z) = L_{\ell m}^E(k) + \Delta L_{\ell m}^E(k, z) \quad (\text{AII.5})$$

The term $\Delta L_{\ell m}^E(k, z)$ results from the elimination procedure and depends on the $\tilde{S}_{\ell m}^E(k, z)$ with $\ell, m > M'$ and on z , through the z on the left-hand sides of the equations with $\ell > M'$. Then the $\tilde{S}_{\ell m}^E(k, z)$ are approximated by the $\tilde{S}_{\ell m}^{E'}(k, z)$ which follow from the approximated equation:

$$z \tilde{S}_{\ell m}^{E'}(k, z) = \sum_{n=1}^{M'} W'_{\ell n}(k) \tilde{S}_{nm}^{E'}(k, z) + \delta_{\ell m} \quad (\text{AII.6})$$

with:

$$W'_{\ell m}(k) = W_{\ell m}(k, 0) = L_{\ell m}^E(k) + \Delta L_{\ell m}^E(k, 0) \quad (\text{AII.7})$$

The $\tilde{S}_{\ell m}^{E'}(k, z)$ are good approximations to the $\tilde{S}_{\ell m}^E(k, z)$, when the z dependence of the $\Delta L_{\ell m}^E(k, z)$ can be neglected. (AII.6) follows from (AII.3) when, in the elimination procedure, one puts $z=0$ on the left hand side of all the equations with $\ell > M'$. This means that it is assumed that the decay time of any of the correlation functions (AII.1) with $\ell, m > M'$ is much faster than that of the functions with $\ell, m \leq M'$. The $M' \times M'$ matrix $W'(k)$ with elements $W'_{\ell m}(k)$ can be obtained by putting $z=0$ in (AII.3). One then obtains:

$$W'(k) = [\tilde{S}^E(k, 0)]^{-1} \quad (\text{AII.8})$$

where $\tilde{S}^E(k, 0)$ is the $M' \times M'$ matrix with elements $\tilde{S}_{\ell m}^E(k, 0)$. This last quantity is usually computed in the BGK approximation of order M with $M > M'$.

The $\tilde{S}_{\ell m}^{E'}(k, z)$ are obtained from (AII.6) as:

$$\tilde{S}_{\ell m}^{E'}(k, z) = \left[\frac{1}{z - W'(k)} \right] \quad (\text{AII.9})$$

from which we see that the M' effective eigenmodes are obtained from the $M' \times M'$ matrix $W'(k)$.

References

- 1) For light scattering see, for example, B. J. Berne and R. Pecora, Dynamic Light Scattering (John Wiley and Sons, New York, 1976).
- 2) For neutron scattering see J. P. Hansen and I. R. McDonald, The Theory of Simple Fluids, (Academic Press, London, 1976).
- 3) S. Chapman and T. G. Cowling, The Mathematical Theory of Nonuniform Gases (Cambridge University Press, Cambridge, 1970); P. Resibois and M. de Leener, Classical Kinetic Theory of Fluids (John Wiley and Sons, New York, 1977).
- 4) S. Harris, An Introduction to the Theory of the Boltzmann Equation (Holt, Rinehart and Winston, New York, 1971).
- 5) B. Kamgar-Parsi, E. G. D. Cohen, and I. M. de Schepper, Phys. Rev. A35, 4781 (1987).
- 6) For a review of linear response theory, see Ref. 2.
- 7) M. H. Ernst, J. R. Dorfman, W. R. Hoegy, and J. M. J. van Leeuwen, Physica 45, 127 (1969).
- 8) H. H. U. Konijnendijk and J. M. J. van Leeuwen, Physica 64, 342 (1973).
- 9) H. van Beijeren and M. H. Ernst, Physica 68, 437 (1973).
- 10) I. M. de Schepper, private communication.
- 11) I. M. de Schepper, E. G. D. Cohen, and B. Kamgar-Parsi, J. Stat. Phys. 54, 273 (1989).
- 12) I. M. de Schepper and E. G. D. Cohen, J. Stat. Phys. 27, 223 (1982).

- 13) See, for example, P. M. Morse and H. Feshbach, Methods of Theoretical Physics (Mc-Graw Hill, New York, 1953).
- 14) H. Grad, in Rarefied Gas Dynamics, edited by F. M. Devienne (Pergamon, New York, 1960), Vol. 3, p. 100.
- 15) R. J. Huck and E. A. Johnson, Phys. Rev. Lett. 44, 142 (1980); Rarefied Gas Dynamics, edited by S. S. Fisher (American Institute of Aeronautics and Astronautics, New York, 1980), Vol. 74, p. 452; J. R. Bowler and E. A. Johnson, Phys Rev. Lett. 54, 329 (1985).
- 16) B. Kamgar-Parsi and E. G. D. Cohen, Int. J. Thermophys. 7, 395 (1986).
- 17) J. Bosse, G. Jacucci, M. Ronchetti, and W. Schirmacher, Phys. Rev. Lett. 57, 3277 (1986).
- 18) L. Letamendia et al., Phys. Rev. A24, 1574 (1981).
- 19) C. Cohen, J. W. H. Sutherland, and J. M. Deutch, Phys. Chem. Liquids 2, 213 (1971).
- 20) H. Mori, Prog. Theor. Phys. 33, 423 (1965), and 34, 399 (1965); R. Zwanzig, in Lectures in Theoretical Physics, edited by W. Brittin and L. Dunham (Wiley-Interscience, New York, 1961), Vol. 3, p. 135.
- 21) W. Montfrooy, P. Westerhuijs, V. O. de Haan, and I. M. de Schepper, preprint, Delft (March 1989).

End