

Linear kinetic theory of the square-well fluid

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 237

(<http://iopscience.iop.org/0953-8984/1/1/020>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.89

The article was downloaded on 10/05/2010 at 15:49

Please note that [terms and conditions apply](#).

Linear kinetic theory of the square-well fluid

Jan A Leegwater[†], Henk van Beijeren[†] and Jan P J Michels[‡]

[†] Instituut voor Theoretische Fysica, Rijksuniversiteit te Utrecht, 3508 TA Utrecht, The Netherlands

[‡] Van der Waals Laboratorium, Universiteit van Amsterdam, Amsterdam, The Netherlands

Received 9 June 1988

Abstract. A recently proposed kinetic theory for a dense fluid of square-well particles is linearised and shown to satisfy time-reversal symmetry. The hydrodynamic modes and their extensions to short wavelengths are calculated with the aid of equilibrium correlation functions which are taken from molecular dynamics simulations and are presented as well. Under most conditions, potential energy fluctuations decay slowly in comparison with velocity fluctuations.

1. Introduction

A long-standing problem in kinetic theory of fluids at moderate and high densities is how to treat the effects of a finite interaction range. The most apparent complications resulting from this are:

- (i) at high densities most of the time particles interact with several particles simultaneously;
- (ii) energy density is not determined by the one-particle distribution function alone since potential energy density is an essential part of it.

One way of dealing with the first complication is to separate the pair potential into a strong repulsive part and a weak tail. The interaction through the repulsive part is treated as an instantaneous hard-sphere-like collision and the interaction through the weak tail is approximated by a mean force obtained by averaging the pair force with the non-equilibrium pair correlation function. The resulting theories, kinetic reference theory and kinetic variational theory (Karkheck and Stell 1981) can be used to obtain quite good predictions for transport coefficients of simple fluids such as noble gases, but there remain a few serious problems. First these theories do not allow for an irreversible exchange of kinetic and potential energy and as a result cannot describe a full relaxation to equilibrium. Secondly their results depend sensitively on the precise choice of the separation between repulsive part and weak tail and there are no clear physical arguments determining this separation uniquely. Another way of avoiding the complications of many-body interactions and keeping a non-zero potential energy density is to consider a system of particles with pairwise square-well interactions. That is, the pair interaction is of the form $\varphi(r_{ij}) = \infty$ if $r_{ij} < \sigma$, $\varphi(r_{ij}) = -\varepsilon$ if $\sigma < r_{ij} < R$ and $\varphi(r_{ij}) = 0$ if $r_{ij} > R$. At

low densities the Boltzmann equation takes into account the full two-body dynamics with the exception of bound states (Karkheck and Stell 1983), but at high densities, in order to make the system tractable one has to ignore correlations between subsequent partial collisions (i.e. collisions either at the inner core $r_{ij} = \sigma$ or at the square-well edge $r_{ij} = R$). If the density is high enough, between two subsequent collisions of a pair ij , each of the particles i and j will most of the time suffer several collisions with other particles (mean free path $\ll R - \sigma$) in which case this assumption seems reasonable. Davis and co-workers were the first to base a kinetic theory on these ideas (Davis *et al* 1961), but their kinetic theory suffers from the problem that energy is not strictly conserved. An improved version avoiding this problem has been derived recently by Karkheck *et al* (1985).

In the present paper we linearise their equations and determine the smallest eigenvalues and corresponding eigenfunctions as a function of wavenumber. One of our remarkable findings is the slowness of the exchange between kinetic and potential energy. Basically this is a non-hydrodynamic process; the decay rate for this process does not tend to zero with vanishing wavenumber. For non-zero wavenumber, however, the decay rate of the eigen-function that is mainly responsible for this decay becomes as small as or even smaller than the decay rates of extended hydrodynamic modes.

The paper is organised as follows: in § 2 we give the kinetic equations of Karkheck *et al*, in § 3 we present some results for the functional derivatives in equilibrium that will be needed, in § 4 we linearise the kinetic equations, in § 5 we calculate their eigenvalues and corresponding eigenfunctions, and in § 6 we state our conclusions.

2. Kinetic theory

The hierarchy equations for the one-particle distribution function $f_1(x, t)$, with $x = (\mathbf{r}, \mathbf{v})$, and the potential energy density

$$u(\mathbf{r}_1, t) = \int d\mathbf{v}_1 \int d\mathbf{x}_2 [\varphi(r_{12})/2] f_2(x_1, x_2, t) \quad (2.1)$$

for the square-well interaction are

$$\partial f_1(x_1, t)/\partial t = -\mathbf{v}_1 \cdot \nabla_1 f_1(x_1, t) + \int d\mathbf{x}_2 \bar{T}_{12} f_2(x_1, x_2, t) \quad (2.2)$$

$$\begin{aligned} \partial u(\mathbf{r}_1, t)/\partial t = & -\nabla_1 \cdot \int d\mathbf{v}_1 \int d\mathbf{x}_2 \mathbf{v}_1 [\varphi(r_{12})/2] f_2(x_1, x_2, t) \\ & + (\varepsilon/2) \int d\mathbf{v}_1 \int d\mathbf{x}_2 |\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}| f_2(x_1, x_2, t) \\ & \times [\Theta(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} - v_e) \delta(r_{12} - R^-) - \Theta(-\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}) \delta(r_{12} - R^+)]. \end{aligned} \quad (2.3)$$

We have adopted the notation of Karkheck *et al* (1985). Closure of these hierarchy equations can be obtained using the maximisation-of-entropy procedure (Karkheck *et al* 1985). In this procedure it is assumed that the phase space density $\rho_N(x_1, \dots, x_N, t)$ is given as

$$\rho_N(x_1, \dots, x_N, t) = \frac{1}{Z_N N!} \exp\left(\sum_{i=1}^N \lambda(x_i, t) - \sum_{i \neq j} \beta(r_{ij}, t) \frac{\varphi(r_{ij})}{2}\right) \quad (2.4)$$

where $\lambda(x, t)$ and $\beta(\mathbf{r}, t)$ are Lagrange multiplier fields that have to be chosen such that the one-particle distribution function $f_1(x, t)$ and the potential energy density $u(\mathbf{r}, t)$ are reproduced correctly. This yields the closure approximation for f_2

$$f_2^{(cl)}(x_1, x_2, t) = f_1(x_1, t)f_1(x_2, t)g_2(r_1, r_2|n, \beta) \quad (2.5)$$

where the pair correlation function g_2 depends functionally on $\beta(\mathbf{r}, t)$ and the local number density $n(\mathbf{r}, t)$. The quantity $\beta(\mathbf{r}, t)$ is the Lagrange multiplier field corresponding to the potential energy (see (2.4)) and $k_B\beta(\mathbf{r}, t)$ can be interpreted as the inverse of the local potential energy temperature. In equilibrium the potential energy temperature equals the kinetic energy temperature, but out of equilibrium the two temperatures are not necessarily the same (van Beijeren *et al* 1988). From (2.5) we see that pre-collisional velocity correlations are not taken into account.

The aim of this paper is to calculate the collective modes of the linearised kinetic theory, which can be distinguished into hydrodynamic modes, their extension to short wavelengths (extended hydrodynamic modes) and kinetic modes. To this end we define deviations from equilibrium through

$$f_1(x, t) = f_1^{eq}(x)[1 + h(x, t)] \quad (2.6)$$

$$n(\mathbf{r}, t) = n^{eq}(\mathbf{r}) + \delta n(\mathbf{r}, t) = n^{eq}(\mathbf{r}) \left(1 + \int d\mathbf{v} h(x, t) \right) \quad (2.7)$$

$$u(\mathbf{r}, t) = u^{eq}(\mathbf{r}) + \delta u(\mathbf{r}, t) \quad (2.8)$$

$$\lambda(\mathbf{r}, t) = \int d\mathbf{v} \lambda(x, t) = \lambda^{eq} + \delta\lambda(\mathbf{r}, t) \quad (2.9)$$

$$\beta(\mathbf{r}, t) = \beta^{eq} + \delta\beta(\mathbf{r}, t). \quad (2.10)$$

Here we have used the fact that in equilibrium λ and β are constant throughout the fluid. In this paper we will only consider fluids that are uniform in equilibrium so also n and u are constant throughout the fluid. We will present the linearised kinetic equations for the independent variables $h(x, t)$ and $\delta\beta(\mathbf{r}, t)$, but first we derive some equilibrium relations that will be needed.

3. Equilibrium results

Up to linear order we have

$$\delta u(\mathbf{r}_1, t) = \int d\mathbf{r}_2 \left(\frac{\delta u(\mathbf{r}_1)}{\delta n(\mathbf{r}_2)} \Big|_{\beta} \delta n(\mathbf{r}_2, t) + \frac{\delta u(\mathbf{r}_1)}{\delta \beta(\mathbf{r}_2)} \Big|_n \delta \beta(\mathbf{r}_2, t) \right) \quad (3.1)$$

or equivalently

$$\delta \beta(\mathbf{r}_1, t) = \int d\mathbf{r}_2 C_u(\mathbf{r}_1, \mathbf{r}_2) \left(\delta u(\mathbf{r}_2, t) - \int d\mathbf{r}_3 \frac{\delta u(\mathbf{r}_2)}{\delta n(\mathbf{r}_3)} \Big|_{\beta} \delta n(\mathbf{r}_3, t) \right) \quad (3.2)$$

where C_u is defined as

$$C_u(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta \beta(\mathbf{r}_1)}{\delta u(\mathbf{r}_2)} \Big|_n. \quad (3.3)$$

Consequently

$$\int d\mathbf{r}_2 C_u(\mathbf{r}_1, \mathbf{r}_2) \left. \frac{\delta u(\mathbf{r}_2)}{\delta \beta(\mathbf{r}_3)} \right|_n = \delta(\mathbf{r}_1 - \mathbf{r}_3). \quad (3.4)$$

The function C_u is similar to a function C_n related to the familiar Ornstein–Zernike direct correlation function $C(\mathbf{r}_1, \mathbf{r}_2)$ as

$$C_n(\mathbf{r}_1, \mathbf{r}_2) = \left. \frac{\delta \lambda(\mathbf{r}_1)}{\delta n(\mathbf{r}_2)} \right|_\beta = \frac{1}{n(\mathbf{r}_1)} \delta(\mathbf{r}_1 - \mathbf{r}_2) - C(\mathbf{r}_1, \mathbf{r}_2). \quad (3.5)$$

Notice that both C_n and C_u are the derivatives of a Lagrange multiplier with respect to its (local) thermodynamic conjugate.

Substituting (2.6), (2.7) and (2.10) into (2.5) we have up to linear order

$$\begin{aligned} f_2^{(\text{lin})}(x_1, x_2, t) = f_2^{\text{eq}}(x_1, x_2) & \left(1 + h(x_1, t) + h(x_2, t) + \int d\mathbf{r}_3 \left. \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_3)} \right|_\beta \delta n(\mathbf{r}_3, t) \right. \\ & \left. + \int d\mathbf{r}_3 \left. \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \beta(\mathbf{r}_3)} \right|_n \delta \beta(\mathbf{r}_3, t) \right). \end{aligned} \quad (3.6)$$

The functional derivatives taken in equilibrium are well defined if for ρ_N we use the explicit form (2.4), obtained from the maximisation-of-entropy procedure. Details of the calculation can be found in Appendix 1. The results are

$$\begin{aligned} \left. \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_3)} \right|_\beta &= \int d\mathbf{r}_4 \left. \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \lambda(\mathbf{r}_4)} \right|_\beta \left. \frac{\delta \lambda(\mathbf{r}_4)}{\delta n(\mathbf{r}_3)} \right|_\beta \\ &= -\frac{g_2(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_3)} [\delta(\mathbf{r}_1 - \mathbf{r}_3) + \delta(\mathbf{r}_2 - \mathbf{r}_3)] \\ &+ \int d\mathbf{r}_4 C_n(\mathbf{r}_3, \mathbf{r}_4) \{ [\delta(\mathbf{r}_1 - \mathbf{r}_4) + \delta(\mathbf{r}_2 - \mathbf{r}_4)] g_2(\mathbf{r}_1, \mathbf{r}_2) \\ &+ n(\mathbf{r}_4) [g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_4) - g_2(\mathbf{r}_1, \mathbf{r}_2)] \} \end{aligned} \quad (3.7)$$

and

$$\begin{aligned} \left. \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \beta(\mathbf{r}_3)} \right|_n &= \frac{1}{n(\mathbf{r}_1)n(\mathbf{r}_2)} \left(\left. \frac{\delta n_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \beta(\mathbf{r}_3)} \right|_\lambda - \int d\mathbf{r}_4 \left. \frac{\delta n_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_4)} \right|_\beta \left. \frac{\delta n(\mathbf{r}_4)}{\delta \beta(\mathbf{r}_3)} \right|_\lambda \right) \\ &= -\frac{1}{2} \int d\mathbf{r}_4 \varphi(\mathbf{r}_3, \mathbf{r}_4) \{ n(\mathbf{r}_3)n(\mathbf{r}_4) [g_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) - g_2(\mathbf{r}_1, \mathbf{r}_2)g_2(\mathbf{r}_3, \mathbf{r}_4)] \\ &+ [\delta(\mathbf{r}_1 - \mathbf{r}_3) + \delta(\mathbf{r}_2 - \mathbf{r}_3)] n(\mathbf{r}_4) g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_4) \\ &+ [\delta(\mathbf{r}_1 - \mathbf{r}_4) + \delta(\mathbf{r}_2 - \mathbf{r}_4)] n(\mathbf{r}_3) g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ &+ [\delta(\mathbf{r}_1 - \mathbf{r}_3)\delta(\mathbf{r}_2 - \mathbf{r}_4) + \delta(\mathbf{r}_1 - \mathbf{r}_4)\delta(\mathbf{r}_2 - \mathbf{r}_3)] g_2(\mathbf{r}_1, \mathbf{r}_2) \} \\ &- \frac{1}{n(\mathbf{r}_1)n(\mathbf{r}_2)} \int d\mathbf{r}_4 \left. \frac{\delta n_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_4)} \right|_\beta \left. \frac{\delta n(\mathbf{r}_4)}{\delta \beta(\mathbf{r}_3)} \right|_\lambda. \end{aligned} \quad (3.8)$$

In a similar way some other functional derivatives can be obtained as

$$\left. \frac{\delta n(\mathbf{r}_1)}{\delta \lambda(\mathbf{r}_2)} \right|_{\beta} = \langle \underline{n}(\mathbf{r}_1) \underline{n}(\mathbf{r}_2) \rangle - n^{(\text{eq})} n^{(\text{eq})} \quad (3.9)$$

$$\begin{aligned} \left. \frac{\delta u(\mathbf{r}_1)}{\delta n(\mathbf{r}_2)} \right|_{\beta} &= \left. \frac{\delta \lambda(\mathbf{r}_2)}{\delta \beta(\mathbf{r}_1)} \right|_n = \int d\mathbf{r}_3 \left. \frac{\delta u(\mathbf{r}_1)}{\delta \lambda(\mathbf{r}_3)} \right|_{\beta} \left. \frac{\delta \lambda(\mathbf{r}_3)}{\delta n(\mathbf{r}_2)} \right|_{\beta} \\ &= \int d\mathbf{r}_3 [\langle \underline{u}(\mathbf{r}_1) \underline{n}(\mathbf{r}_3) \rangle - u^{(\text{eq})} n^{(\text{eq})}] C_n(\mathbf{r}_3, \mathbf{r}_2) \end{aligned} \quad (3.10)$$

and

$$\begin{aligned} \left. \frac{\delta u(\mathbf{r}_1)}{\delta \beta(\mathbf{r}_2)} \right|_n &= \left. \frac{\delta u(\mathbf{r}_1)}{\delta \beta(\mathbf{r}_2)} \right|_{\lambda} - \int d\mathbf{r}_3 \left. \frac{\delta u(\mathbf{r}_1)}{\delta n(\mathbf{r}_3)} \right|_{\beta} \left. \frac{\delta n(\mathbf{r}_3)}{\delta \beta(\mathbf{r}_2)} \right|_{\lambda} \\ &= -[\langle \underline{u}(\mathbf{r}_1) \underline{u}(\mathbf{r}_2) \rangle - u^{(\text{eq})} u^{(\text{eq})}] + \int d\mathbf{r}_3 \int d\mathbf{r}_4 [\langle \underline{u}(\mathbf{r}_1) \underline{n}(\mathbf{r}_3) \rangle - u^{(\text{eq})} n^{(\text{eq})}] \\ &\quad \times C_n(\mathbf{r}_3, \mathbf{r}_4) [\langle \underline{u}(\mathbf{r}_2) \underline{n}(\mathbf{r}_4) \rangle - u^{(\text{eq})} n^{(\text{eq})}]. \end{aligned} \quad (3.11)$$

Here $\langle \dots \rangle$ denotes an equilibrium average and \underline{n} and \underline{u} are the microscopic number density and potential energy density

$$\underline{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (3.12)$$

$$\underline{u}(\mathbf{r}) = \frac{1}{2} \sum_{i \neq j}^N \delta(\mathbf{r} - \mathbf{r}_i) \varphi(r_{ij}). \quad (3.13)$$

We still have to solve (3.5) and (3.4) in order to express C_n and C_u in terms of the correlation functions $\langle \underline{n}\underline{n} \rangle$, $\langle \underline{n}\underline{u} \rangle$ and $\langle \underline{u}\underline{u} \rangle$. In a spatially inhomogeneous fluid this is a difficult problem; in the homogeneous case it is fairly straightforward if one uses Fourier transforms.

Defining the Fourier transform of an arbitrary function A of \mathbf{r} as

$$A(\mathbf{k}) = \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} A(\mathbf{r})$$

and combining the relations (3.5) and (3.9) we find for C_n

$$\int d\mathbf{k}' \langle \underline{n}(\mathbf{k}) \underline{n}(\mathbf{k}') \rangle C_n(\mathbf{k}', \mathbf{k}'') = \delta(\mathbf{k} - \mathbf{k}''). \quad (3.14)$$

For a uniform fluid one has

$$\langle \underline{n}(\mathbf{k}) \underline{n}(\mathbf{k}') \rangle = \delta(\mathbf{k} + \mathbf{k}') \langle \underline{n}(\mathbf{k}) \underline{n}(-\mathbf{k}) \rangle \quad (3.15)$$

so

$$C_n(\mathbf{k}, \mathbf{k}') = \frac{\delta(\mathbf{k} + \mathbf{k}')}{\langle \underline{n}(\mathbf{k}) \underline{n}(-\mathbf{k}) \rangle}. \quad (3.16)$$

If we define

$$\bar{S}_{\varphi}(\mathbf{k}) = \langle \underline{u}(\mathbf{k}) \underline{u}(-\mathbf{k}) \rangle - \frac{\langle \underline{n}(\mathbf{k}) \underline{u}(-\mathbf{k}) \rangle^2}{\langle \underline{n}(\mathbf{k}) \underline{n}(-\mathbf{k}) \rangle} \quad (3.17)$$

the analogue for C_u becomes

$$C_u(\mathbf{k}, \mathbf{k}') = -\frac{\delta(\mathbf{k} + \mathbf{k}')}{\bar{S}_\varphi(k)}. \quad (3.18)$$

We want to stress that the use of a Fourier transform essentially depends on the uniformity of the fluid. Solving (3.5) and (3.4) for a non-uniform fluid is difficult, even if the correlation functions $\langle \underline{n} \underline{n} \rangle$, $\langle \underline{n} \underline{u} \rangle$ and $\langle \underline{u} \underline{u} \rangle$ are known.

For a uniform fluid the required correlation functions are

$$S(k) = \frac{\langle \underline{n}(k) \underline{n}(-k) \rangle}{N} \quad (3.19)$$

$$S_u(k) = \frac{\langle \underline{n}(k) \underline{u}(-k) \rangle}{V_{u^{(eq)}}} - \frac{\langle \underline{n}(k) \underline{n}(-k) \rangle}{V_{n^{(eq)}}} \quad (3.20)$$

and

$$S_\varphi = \bar{S}_\varphi / u^{(eq)2} V. \quad (3.21)$$

As far as we are aware there is no equilibrium theory available for the correlation functions S_u and S_φ . One of us (JM) has obtained them from molecular dynamics simulations. The method and further details have been described elsewhere (Michels and Trappeniers 1980). Typical results for three temperatures at $n\sigma^3 = 0.8$ and three densities at $\beta\varepsilon = 0.667$ are presented in figures 1–6.

4. The linearised kinetic equations

Substitution of (2.6), (3.6), (3.7) and (3.8) in (2.2) and (2.3) yields the linearised kinetic equations for the one-particle distribution function,

$$\begin{aligned} n_0 f_m(\mathbf{v}_1) \left(\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \nabla_1 \right) h(x_1, t) \\ = \int d\mathbf{x}_2 \bar{T}_{12} f_2^{(eq)}(x_1, x_2) \left(h(x_1, t) + h(x_2, t) \right. \\ \left. + \int d\mathbf{r}_3 \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_3)} \Big|_\beta \delta n(\mathbf{r}_3, t) + \int d\mathbf{r}_3 \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \beta(\mathbf{r}_3)} \Big|_n \delta \beta(\mathbf{r}_3, t) \right) \end{aligned} \quad (4.1)$$

and for the potential energy density

$$\begin{aligned} \frac{\partial}{\partial t} \delta u(\mathbf{r}_1, t) = -\nabla_1 \cdot \int d\mathbf{v}_1 \int d\mathbf{x}_2 \mathbf{v}_1 \frac{\varphi(r_{12})}{2} f_2^{(eq)}(x_1, x_2) h(x_1, t) \\ + (\varepsilon/2) \int d\mathbf{v}_1 \int d\mathbf{x}_2 |\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}| f_2^{(eq)}(x_1, x_2) \\ \times [\Theta(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} - v_e) \delta(r_{12} - R^-) - \Theta(-\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}) \delta(r_{12} - R^+)] \\ \times \left(h(x_1, t) + h(x_2, t) + \int d\mathbf{r}_3 \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_3)} \Big|_\beta \delta n(\mathbf{r}_3, t) \right. \\ \left. + \int d\mathbf{r}_3 \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \beta(\mathbf{r}_3)} \Big|_n \delta \beta(\mathbf{r}_3, t) \right) \end{aligned} \quad (4.2)$$

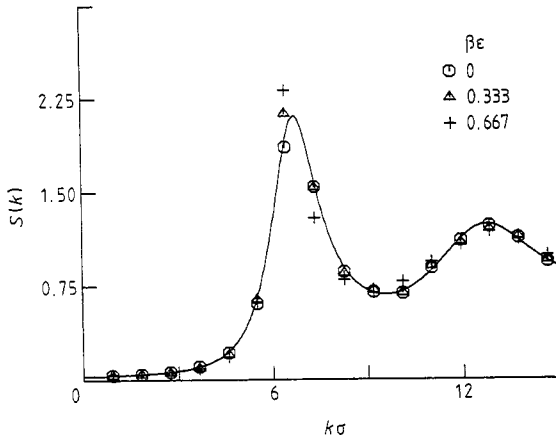


Figure 1. The Fourier transform of the pair correlation function $S(k)$ at $n\sigma^3 = 0.8$, $R = 1.5\sigma$ for three well depths. Full curve: Percus-Yevick approximation for the hard-sphere pair correlation function.

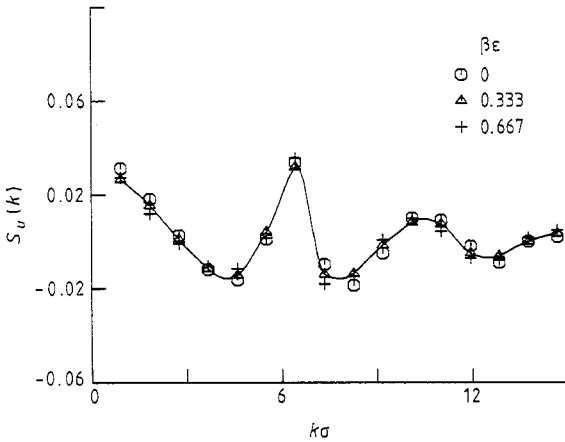


Figure 2. The correlation function $S_u(k)$ at $n\sigma^3 = 0.8$, $R = 1.5\sigma$ for three well depths. The full curve is an interpolation for $\beta\epsilon = \frac{1}{3}$.

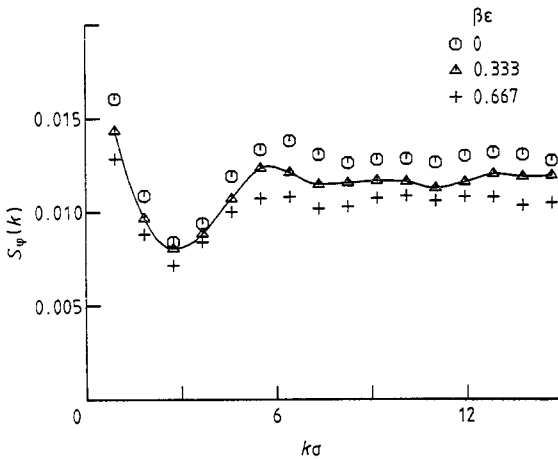


Figure 3. The correlation function $S_v(k)$ at $n\sigma^3 = 0.8$, $R = 1.5\sigma$ for three well depths.

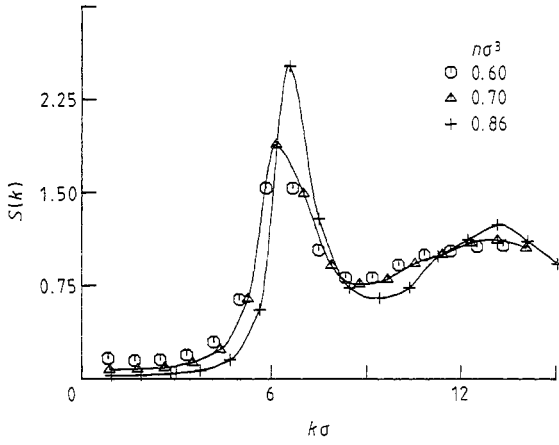


Figure 4. The Fourier transform of the pair correlation function $S(k)$ at $\beta\varepsilon = 0.667$, $R = 1.5\sigma$ for three densities. The full curves are numerical interpolations.

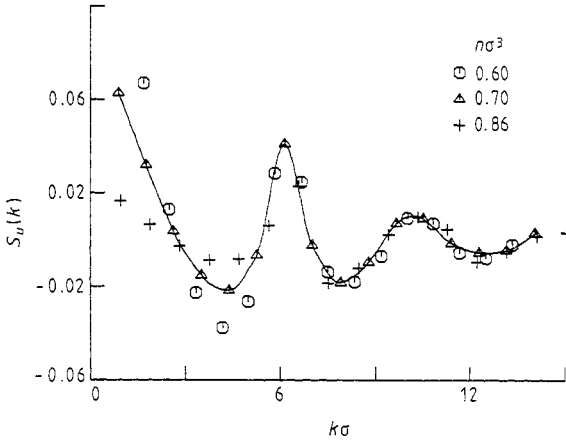


Figure 5. The correlation function $S_u(k)$ at $\beta\varepsilon = 0.667$, $R = 1.5\sigma$ for three densities.

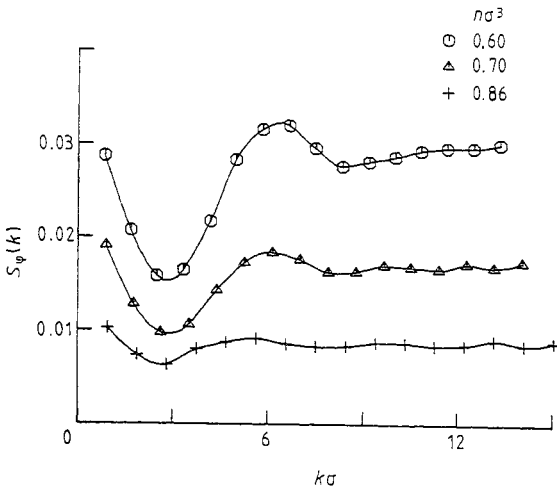


Figure 6. The correlation function $S_\phi(k)$ at $\beta\varepsilon = 0.667$, $R = 1.5\sigma$ for three densities.

where $n_0 = n^{(\text{eq})}$ and f_m is the Maxwell–Boltzmann velocity distribution. In Appendix 2 we show how these can be simplified considerably by using the square-well analogue of the BGY hierarchy, the equilibrium version of the BBGKY hierarchy. A similar simplification has been obtained before for the revised Enskog equation (van Beijeren and Ernst 1973). Using $\delta\beta$ instead of δu as independent variable we obtain as final forms for the linearised kinetic equations

$$\begin{aligned} \frac{\partial}{\partial t} \delta\beta(\mathbf{r}_1, t) = & \int d\mathbf{r}_2 C_u(\mathbf{r}_1, \mathbf{r}_2) \left[\int d\mathbf{r}_3 \left(n_0 \frac{\delta u(\mathbf{r}_2)}{\delta n(\mathbf{r}_3)} \Big|_{\beta} \right. \right. \\ & \left. \left. - u_0 \delta(\mathbf{r}_2 - \mathbf{r}_3) \right) \nabla_3 \cdot \int d\mathbf{v}_3 \mathbf{v}_3 h(\mathbf{r}_3, t) f_m(v_3) \right. \\ & + (\varepsilon/2) \int d\mathbf{v}_2 \int d\mathbf{x}_3 |\mathbf{v}_{23} \cdot \hat{\mathbf{r}}_{23}| [h(\mathbf{x}_2, t) + h(\mathbf{x}_3, t)] \delta(r_{23} - R) \\ & \times n_0^2 f_m(v_2) f_m(v_3) g_2(R^-) [\Theta(\mathbf{v}_{23} \cdot \hat{\mathbf{r}}_{23} - v_e) - e^{-\beta\varepsilon} \Theta(-\mathbf{v}_{23} \cdot \hat{\mathbf{r}}_{23})] \\ & \left. \left. + \frac{\varepsilon^2 e^{-\beta\varepsilon} n_0^2 g_2(R^-)}{4(\beta m \pi)^{1/2}} \int d\mathbf{r}_3 \delta(r_{23} - R) [\delta\beta(\mathbf{r}_2, t) + \delta\beta(\mathbf{r}_3, t)] \right] \quad (4.3) \end{aligned}$$

and

$$\begin{aligned} n_0 f_m(v_1) \left(\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \nabla_1 \right) h(\mathbf{x}_1, t) \\ = \int d\mathbf{x}_2 \bar{T}_{12} f_2^{(\text{eq})}(\mathbf{x}_1, \mathbf{x}_2) \left(h(\mathbf{x}_1, t) - \frac{\delta n(\mathbf{r}_1, t)}{n_0} + h(\mathbf{x}_2, t) - \frac{\delta n(\mathbf{r}_2, t)}{n_0} \right) \\ + f_m(v_1) \mathbf{v}_1 \cdot \nabla_1 \left[\delta n(\mathbf{r}_1, t) - n_0 \int d\mathbf{r}_2 C_n(\mathbf{r}_1, \mathbf{r}_2) \delta n(\mathbf{r}_2, t) \right. \\ \left. - \int d\mathbf{r}_2 \left(n_0 \frac{d\lambda(\mathbf{r}_1)}{\delta\beta(\mathbf{r}_2)} \Big|_n - u_0 \delta(\mathbf{r}_1 - \mathbf{r}_2) \right) \delta\beta(\mathbf{r}_2, t) \right] \\ + n_0^2 (\varepsilon/2) \int d\mathbf{x}_2 f_m(v_1) f_m(v_2) \delta(r_{12} - R) |\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}| g_2(R^+) \\ \times [\delta\beta(\mathbf{r}_1, t) + \delta\beta(\mathbf{r}_2, t)] [\Theta(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} - v_e) - e^{-\beta\varepsilon} \Theta(-\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12})] \quad (4.4) \end{aligned}$$

where $u_0 = u^{(\text{eq})}$. Here we only consider spatially uniform fluids, hence each wavelength may be considered separately. The Fourier transforms of (4.3) and (4.4) are

$$\begin{aligned} \frac{\partial}{\partial t} \delta\beta(\mathbf{k}, t) = & -i\mathbf{k} \cdot \frac{n_0 S_u(k)}{u_0 S_\varphi(k) S(k)} \int d\mathbf{v}_3 \mathbf{v}_3 h(\mathbf{k}, v_3, t) f_m(v_3) \\ & - \frac{n_0^2 \varepsilon}{2 S_\varphi(k) u_0^2} g_2(R^-) \int d\mathbf{r}_{23} \int d\mathbf{v}_2 \int d\mathbf{v}_3 |\mathbf{v}_{23} \cdot \hat{\mathbf{r}}_{23}| \\ & \times [h(\mathbf{k}, v_2, t) + h(\mathbf{k}, v_3, t) \exp(-i\mathbf{k} \cdot \mathbf{r}_{23})] \\ & \times \delta(r_{23} - R) f_m(v_2) f_m(v_3) [\Theta(\mathbf{v}_{23} \cdot \hat{\mathbf{r}}_{23} - v_e) \\ & - e^{-\beta\varepsilon} \Theta(-\mathbf{v}_{23} \cdot \hat{\mathbf{r}}_{23})] - \frac{\varepsilon^2 e^{-\beta\varepsilon} n_0^2 g_2(R^-)}{4 S_\varphi(k) u_0^2 (\beta m \pi)^{1/2}} \\ & \times \int d\mathbf{r}_{23} \delta(r_{23} - R) [1 + \exp(-i\mathbf{k} \cdot \mathbf{r}_{23})] \delta\beta(\mathbf{k}, t) \quad (4.5) \end{aligned}$$

and

$$\begin{aligned}
 & f_m(v_1) \frac{\partial}{\partial t} h(\mathbf{k}, \mathbf{v}_1, t) \\
 &= -i\mathbf{k} \cdot \mathbf{v}_1 f_m(v_1) h(\mathbf{k}, \mathbf{v}_1, t) + n_0 \int d\mathbf{r}_{12} \int d\mathbf{v}_2 \bar{T}_{12} g_2(r_{12}) f_m(v_1) f_m(v_2) \\
 & \quad \times \left[h(\mathbf{k}, \mathbf{v}_1, t) - \frac{\delta n(\mathbf{k}, t)}{n_0} + \exp(-i\mathbf{k} \cdot \mathbf{r}_{12}) \left(h(\mathbf{k}, \mathbf{v}_2, t) - \frac{\delta n(\mathbf{k}, t)}{n_0} \right) \right] \\
 & \quad + i\mathbf{k} \cdot \mathbf{v}_1 f_m(v_1) \left(1 - \frac{1}{S(k)} \right) \frac{\delta n(\mathbf{k}, t)}{n_0} - i\mathbf{k} \cdot \mathbf{v}_1 f_m(v_1) \frac{u_0 S_u(k)}{n_0 S(k)} \delta\beta(\mathbf{k}, t) \\
 & \quad + n_0(\varepsilon/2) \int d\mathbf{r}_{12} \int d\mathbf{v}_2 f_m(v_1) f_m(v_2) \delta(r_{12} - R) |\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}| g_2(R^-) \\
 & \quad \times [1 + \exp(-i\mathbf{k} \cdot \mathbf{r}_{12})] \delta\beta(\mathbf{k}, t) [\Theta(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} - v_c) \\
 & \quad - e^{-\beta\varepsilon} \Theta(-\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12})] \tag{4.6}
 \end{aligned}$$

where we have used (3.10), (3.11), (3.16), (3.18) and (3.21). These equations are of the form

$$\frac{\partial}{\partial t} \begin{pmatrix} h \\ \delta\beta \end{pmatrix} = L \begin{pmatrix} h \\ \delta\beta \end{pmatrix}. \tag{4.7}$$

Because of its resemblance to the Enskog operator for hard spheres we will call L the Enskog-like operator.

5. The collective modes

The kinetic equations are linear, so one can consider the eigen-functions of L . As there are five conserved quantities (particle number, momentum and total energy) we know that, if the linear kinetic equations are to obey the conservation laws, five eigenvalues will tend to zero as k tends to zero. Partly because potential energy density is treated explicitly, this can indeed be shown to be the case.

We will use the so-called moment method (Kamgar Parsi and Cohen 1986) to obtain approximate solutions of the linearised kinetic equations. The first step is the expansion of $h(\mathbf{k}, \mathbf{v}, t)$ in a set of polynomials

$$h(\mathbf{k}, \mathbf{v}, t) = \sum_{rlm} h_{rlm}(\mathbf{k}, t) \psi_{rlm}(\mathbf{v}) \tag{5.1}$$

where we have chosen the polynomials ψ as

$$\psi_{rlm}(\mathbf{v}) = N_{rl} L_r^{l+1/2}(v^2) v^l Y_{lm}(\hat{\mathbf{v}}). \tag{5.2}$$

Here L_r is the associated Laguerre or Sonine polynomial, Y_{lm} is a spherical harmonic and N_{rl} a normalisation constant. This is a standard choice (Kamgar Parsi and Cohen 1986). Because of rotational invariance around \mathbf{k} we may consider each value of m separately. We now define an inner product as an equilibrium expectation value

$$\langle \psi_a | \psi_b \rangle = \langle \hat{\Phi}_a^* \hat{\Phi}_b \rangle \tag{5.3}$$

where we have introduced

$$\hat{\Phi}_{rlm}(x_1, \dots, x_N) = \frac{1}{\sqrt{N}} \sum_{i=1}^N \psi_{rlm}(\mathbf{v}_i) \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}_i) \quad (5.4)$$

and

$$\begin{aligned} \hat{\Phi}_\beta(x_1, \dots, x_N) &= \frac{C_u(k)}{\sqrt{N}} \left(\int d\mathbf{r} \underline{u}(\mathbf{r}) \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}) - \int d\mathbf{r} \int d\mathbf{r}' \left. \frac{\delta u(\mathbf{r})}{\delta n(\mathbf{r}')} \right|_\beta \underline{n}(\mathbf{r}') \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}) \right) \\ &= \frac{C_u(k)}{\sqrt{N}} \left(\sum_{i \neq j} \frac{\varphi(r_{ij})}{2} \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}_i) - \sum_{i=1}^N \int d\mathbf{r} \left. \frac{\delta u(\mathbf{r})}{\delta n(\mathbf{r}_i)} \right|_\beta \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}_i) \right). \end{aligned} \quad (5.5)$$

The expression (5.5) is inferred from equation (3.2). The $\hat{\Phi}_a$ are orthogonal, that is

$$\langle \hat{\Phi}_a | \hat{\Phi}_b \rangle = c_a \delta_{ab} \quad (5.6)$$

for instance

$$\begin{aligned} \langle \hat{\Phi}_n | \hat{\Phi}_\beta \rangle &= \langle \hat{\Phi}_{000}^* | \hat{\Phi}_\beta \rangle \\ &= C_u(k) \left\langle n\underline{u} - \left. \frac{\delta u}{\delta n} \right|_\beta n\underline{n} \right\rangle \\ &= 0 \end{aligned} \quad (5.7)$$

(cf. (3.10) and (3.5)). It is straightforward to show that

$$c_a = 1 \quad \text{all } (rlm) \text{ except } (000) \sim n \quad (5.8)$$

$$c_n = S(k) \quad (5.9)$$

$$c_\beta = C_u(k). \quad (5.10)$$

The inner product defined by (5.3) is a natural choice, so in the sequel of this paper we will use a basis normalised with respect to fluctuations

$$\Phi_a(x_1, \dots, x_N) = \frac{1}{\sqrt{c_a}} \hat{\Phi}_a(x_1, \dots, x_N). \quad (5.11)$$

Since the polynomials ψ are complete in the space of square-integrable functions, the linearised kinetic equations are formally equivalent to

$$\frac{\partial}{\partial t} h_i(t) = \sum_j L_{ij}(\mathbf{k}) h_j(t) \quad i, j = \beta, (rlm) \quad (5.12)$$

where we have used the notation $h_\beta = \delta\beta$. With respect to the unhatted basis the Enskog-like operator can be shown to satisfy the symmetry relation

$$L_{ab}(\mathbf{k}) = \varepsilon_a \varepsilon_b L_{ba}^*(\mathbf{k}) \quad (5.13)$$

where

$$\varepsilon_a = \begin{cases} 1 & \text{for } \beta \text{ and for } l \text{ even} \\ -1 & \text{for } l \text{ odd.} \end{cases}$$

This is due to the fact that the closure approximation (2.4) does not break time-reversal symmetry. Perhaps the most straightforward way to see this is by noting that the linear

kinetic equations can also be derived by using standard projection operators. The Enskog-like operator can also be derived as

$$L_{ab}(\mathbf{k}) = \langle \Phi_a^* L \Phi_b \rangle \tag{5.14}$$

where L is the pseudo-Liouville operator (Karkheck *et al* 1985). This relation has been introduced by Konijnendijk and van Leeuwen (1973) by methods similar to ours, whereas Cohen and de Schepper (1987) arrived at the same results but defined their inner product with the aid of pair correlation functions instead of N -body averages. Our method generalises this to arbitrary Liouville and pseudo-Liouville operators and arbitrary phase functions Φ_a .

We have written a computer program to calculate the matrix elements of the Enskog-like operator. The first few matrix elements are given in table 1.

We have obtained approximate solutions of (4.5) and (4.6) by considering only a finite submatrix of L and computing the eigenvalues and eigenfunctions numerically. This is called the moment method. We have chosen this method, as our main interest here is to study the kinetic equations (4.5) and (4.6) in the long- and intermediate-wavelength regime at high densities. It is known (Kamgar Parsi and Cohen 1986) that the moment method works quite well in this regime.

In figure 7 we give the eigenvalues z_j of the lowest-lying longitudinal ($m = 0$) modes multiplied by $t_E = t_0/g(\sigma)$. Notice that t_E is the mean free time between collisions at the hard core. Among the modes are the heat mode, two sound modes and their extensions to finite wavelengths, kinetic modes and a mode describing mainly the exchange of kinetic and potential energy. This exchange mode is not present in the Boltzmann equation or the Enskog equation.

Table 1. Some matrix elements of the Enskog-like operator.

a	b	L_{ab}
n	010	$-\frac{\lambda_f}{\sqrt{S(k)}}$
n	other	0
β	β	$-\frac{e^{-\beta\varepsilon}}{4S_\varphi(k)}\lambda_R[1 + j_0(kR)]$
β	010	$-\frac{S_u(k)}{S(k)\sqrt{S_\varphi(k)}}\lambda_f - \frac{\lambda_R}{\sqrt{S_\varphi(k)}}\Lambda\frac{ij_1(kR)}{2}$
β	100	$-\frac{\lambda_R}{\sqrt{S_\varphi(k)}}\frac{\beta\varepsilon e^{-\beta\varepsilon}}{\sqrt{6}}\frac{1 + j_0(kR)}{2}$
010	010	$-\frac{2}{3}\lambda_\sigma[1 - j_0(k\sigma) + 2j_2(k\sigma)] - \frac{2}{3}\lambda_R\Xi[1 - j_0(kR) + 2j_2(kR)]$
010	100	$-\sqrt{\frac{2}{3}}\lambda_f - i\sqrt{(\pi/6)}j_1(k\sigma)\lambda_\sigma + i(1/\sqrt{6})[\sqrt{\pi}(1 - e^{-\beta\varepsilon}) - \beta\varepsilon\Lambda]j_1(kR)\lambda_R$
100	100	$-\frac{2}{3}\lambda_\sigma[1 - j_0(k\sigma)] - \frac{2}{3}\lambda_R\Xi[1 - j_0(kR)] - \lambda_R[(\beta\varepsilon)^2/6]e^{-\beta\varepsilon}[1 + j_0(kR)]$

$$\lambda_f = \frac{ik}{\sqrt{\beta m}} \qquad t_0 = \sqrt{\frac{\beta m}{\pi}} \frac{1}{4\sigma^2 n_0}$$

$$\lambda_\sigma = \frac{g(\sigma)}{t_0} \qquad \Xi = 1 - \frac{\beta\varepsilon}{2} \left[K_1\left(\frac{\beta\varepsilon}{2}\right) e^{-\beta\varepsilon/2} + e^{-\beta\varepsilon} \right]$$

$$\lambda_R = \frac{g(R^-)R^2}{t_0\sigma^2} \qquad \Lambda = \frac{\sqrt{\pi}}{2} [\operatorname{erfc}(\sqrt{\beta\varepsilon} + e^{-\beta\varepsilon}) + \sqrt{\beta\varepsilon} e^{-\beta\varepsilon}].$$

Here j_n is a spherical Bessel function; K_n is a modified Bessel function.

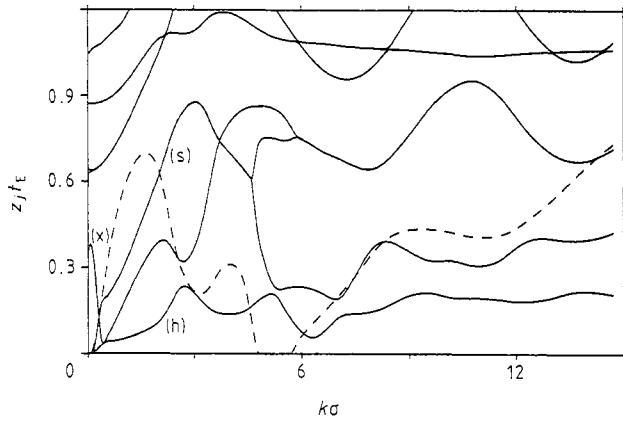


Figure 7. Reduced real (full curves) and imaginary (broken curve) parts of the lowest-lying longitudinal ($m = 0$) modes as a function of reduced wavenumber using the full linear kinetic equations. Here $\beta\epsilon = 0.667$, $R = 1.5\sigma$ and $n\sigma^3 = 0.8$. For k tending to zero we have identified the heat mode (h), two complex conjugate sound modes (s), and the energy exchange mode (x). Only for the extended sound modes, is the imaginary part of the eigenvalue given.

In our calculations we have used the 17×17 dimensional part of the Enskog-like operator on the basis (β, Φ_{r0}) where $(2r + 1) \leq 6$. By varying the number of polynomials we estimated the accuracy of our results. The low-lying (extended hydrodynamic and exchange) modes were found to be accurate up to a few per cent. We did not extend our calculations beyond $k\sigma \sim 14$, owing to convergence problems. In figure 8 we give the absolute values of components of the lowest-lying modes along the normalised base vectors indicated. In figure 9 we present the eigenvalues that are obtained if one sets the potential energy density to be equal to its equilibrium value at all times. In this case total energy is no longer conserved, which is manifested by the fact that only *two* longitudinal modes tend to zero as k tends to zero. Finally in figure 10 we show the eigenvalues at a lower density.

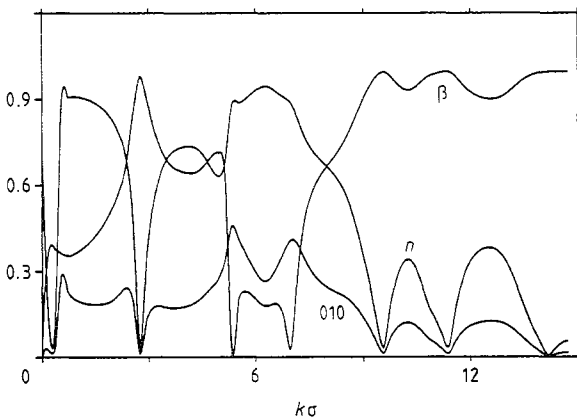


Figure 8. Absolute values of the projections of the mode eigenfunctions of the lowest-lying mode along the normalised base vectors indicated for fluid parameters as in figure 7.

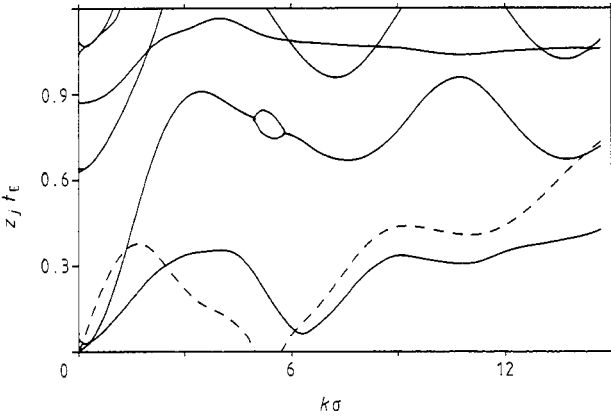


Figure 9. Reduced real (full curves) and imaginary (broken curve) parts of the lowest-lying longitudinal modes using the linear kinetic equations, but keeping the component along β zero. Energy non-conservation is manifested by the fact that only two modes tend to zero as k tends to zero. Near $k = 0$ the real parts of the three lowest-lying eigenvalues cross each other.

6. Discussion

The most important observation is that the inclusion of potential energy in the kinetic equations has a strong influence. This can be seen by comparing figure 7 to figure 9. For all wavelengths considered the kinetic mode describing the exchange of kinetic and potential energy (exchange mode) and its extension to small wavelengths decays slower than any other kinetic mode. For large wavelengths, however, the difference is not that large. The decay rate of the exchange mode falls off very rapidly with k so that even for relatively long wavelengths it becomes as small as or smaller than the decay rate of the hydrodynamic modes. This implies that the applicability of the Chapman–Enskog procedure is restricted to really hydrodynamic wavelengths. As is the case for the revised

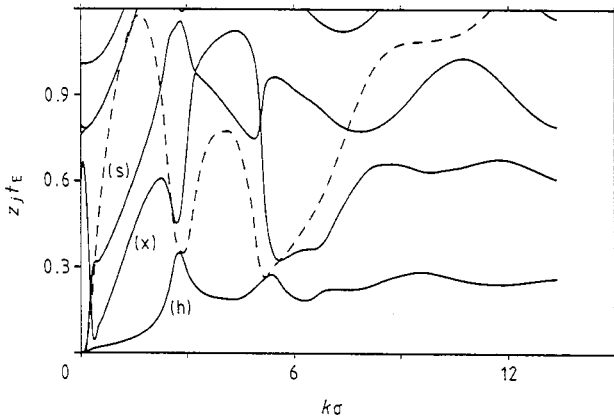


Figure 10. As in figure 7 but here $n\sigma^3 = 0.6$.

Enskog equation for hard spheres, there is a pronounced minimum in the extended heat mode decay rate at $k\sigma \sim 2\pi$. A study of the projection of the modes reveals that in the neighbourhood of the minimum the eigenfunction is almost the number density (unit function). The mechanism that causes this minimum is the same for hard spheres and a square well; deviations from equilibrium of the local density can decay through diffusion only. From table 1 it can be seen that a factor of $1/\sqrt{S(k)}$ is involved, which has a minimum at $k\sigma \sim 2\pi$.

For even shorter wavelengths the extended exchange mode is found to be almost identical to the potential energy temperature, which essentially decouples from one-particle quantities. However, some reservation is called for, as the moment method becomes unreliable at very short wavelengths. There a better approach would be using the BGK method.

Preliminary results of molecular dynamics (MD) simulations on a square-well fluid indeed show evidence for the presence of a low-lying exchange mode, but no such mode has been found in simulations for a Lennard-Jones fluid at high densities (de Schepper *et al* 1988). Therefore the low-lying mode may be a peculiarity of the square-well interaction. Further analysis is in progress of the eigenvalues and eigen-modes in the decay spectrum of equilibrium time correlation functions as obtained from MD simulations on the square-well fluid. A comparison between these and our theoretical predictions will be made in a forthcoming paper.

In addition we will use the results obtained here in an extended mode coupling calculation for the velocity and stress tensor autocorrelation functions (de Schepper *et al* 1986, Kirkpatrick and Nieuwoudt 1986). Since the shear viscosity depends strongly on the depth of the square well (Michels and Trappeniers 1980), this ought to provide a sensitive test of extended mode coupling theory.

Acknowledgments

Two of us (JL and HvB) thank the SUNY at Stony Brook for its hospitality during a visit. We also owe thanks to G Stell and J Karkheck for useful suggestions and H Rynja for useful comments. This work was partly supported by the NATO Research Grant No 419/82 and NSF Grant CHE 8421124.

Appendix 1. Calculation of the functional derivatives

The pair correlation function g_2 is defined as

$$g_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)n(\mathbf{r}_2)} \tag{A1.1}$$

where

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int d\mathbf{v}_1 d\mathbf{v}_2 dx_3 \dots dx_N \rho_N(x_1, \dots, x_N | \lambda, \beta). \tag{A1.2}$$

Using (2.4) for ρ_N we find that

$$\begin{aligned}
 \left. \frac{\delta n_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \lambda(\mathbf{r})} \right|_{\beta} &= N(N-1) \int d\mathbf{v}_1 d\mathbf{v}_2 dx_3 \dots dx_N \left. \frac{\delta \rho_N(x_1, \dots, x_N | \lambda, \beta)}{\delta \lambda(\mathbf{r})} \right|_{\beta} \\
 &= N(N-1) \int d\mathbf{v}_1 d\mathbf{v}_2 dx_3 \dots dx_N \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \rho_N(x_1, \dots, x_N | \lambda, \beta) \\
 &\quad - n_2(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}) \\
 &= [\delta(\mathbf{r} - \mathbf{r}_1) + \delta(\mathbf{r} - \mathbf{r}_2)] n_2(\mathbf{r}_1, \mathbf{r}_2) + n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}) \\
 &\quad - n_2(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}). \tag{A1.3}
 \end{aligned}$$

Now (3.7) follows. Similarly we have

$$\begin{aligned}
 \left. \frac{\delta n_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \beta(\mathbf{r})} \right|_{\lambda} &= N(N-1) \int d\mathbf{v}_1 d\mathbf{v}_2 dx_3 \dots dx_N \left. \frac{\delta \rho_N(x_1, \dots, x_N | \lambda, \beta)}{\delta \beta(\mathbf{r})} \right|_{\lambda} \\
 &= -\frac{1}{2} N(N-1) \int d\mathbf{v}_1 d\mathbf{v}_2 dx_3 \dots dx_N \\
 &\quad \times \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \varphi(r_{ij}) \rho_N(x_1, \dots, x_N | \lambda, \beta) + n_2(\mathbf{r}_1, \mathbf{r}_2) u(\mathbf{r}) \\
 &= \frac{1}{2} N(N-1) \int d\mathbf{r}' \varphi(|\mathbf{r} - \mathbf{r}'|) \int d\mathbf{v}_1 d\mathbf{v}_2 dx_3 \dots dx_N \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \\
 &\quad \times \delta(\mathbf{r}' - \mathbf{r}_j) \rho_N(x_1, \dots, x_N | \lambda, \beta) + n_2(\mathbf{r}_1, \mathbf{r}_2) u(\mathbf{r}) \tag{A1.4}
 \end{aligned}$$

from which the various terms in (3.8) can be found.

Appendix 2. Simplification of the linear kinetic equations

Here we will show how the last two terms in (4.1) are simplified. Using (3.7) we obtain

$$\begin{aligned}
 &\int dx_2 \int d\mathbf{r}_3 \bar{T}_{12} f_m(v_1) f_m(v_2) \left. \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_3)} \right|_{\beta} \delta n(\mathbf{r}_3) \\
 &= - \int dx_2 \int d\mathbf{r}_3 \bar{T}_{12} f_2^{(\text{eq})}(x_1, x_2) \left(\frac{\delta n(\mathbf{r}_1)}{n(\mathbf{r}_1)} + \frac{\delta n(\mathbf{r}_2)}{n(\mathbf{r}_2)} \right) \\
 &\quad + \int dx_2 \int dx_4 \int d\mathbf{r}_3 C_n(\mathbf{r}_3, \mathbf{r}_4) \delta n(\mathbf{r}_3) \bar{T}_{12} \\
 &\quad \times \{ [\delta(\mathbf{r}_1 - \mathbf{r}_4) + \delta(\mathbf{r}_2 - \mathbf{r}_4)] f_2^{(\text{eq})}(x_1, x_2) f_m(v_4) \\
 &\quad + f_3^{(\text{eq})}(x_1, x_2, x_4) - f_2^{(\text{eq})}(x_1, x_2) f_1(x_4) \} \tag{A2.1}
 \end{aligned}$$

where an integration over v_4 has been inserted and we have used the fact that \bar{T}_{12} commutes with any velocity-independent function that is continuous in r_{12} . The second BBGKY equation evaluated in equilibrium can be written as

$$(\mathbf{v}_1 \cdot \nabla_1 + \mathbf{v}_2 \cdot \nabla_2 - \bar{T}_{12}) f_2^{(\text{eq})}(x_1, x_2) = \int dx_3 (\bar{T}_{13} + \bar{T}_{23}) f_3^{(\text{eq})}(x_1, x_2, x_3). \tag{A2.2}$$

Using (A2.2) the second term of (A2.1) becomes

$$\begin{aligned}
 & \int dx_2 \int dr_3 \int dx_4 C_n(\mathbf{r}_3, \mathbf{r}_4) \delta n(\mathbf{r}_3) \bar{T}_{12} [\delta(\mathbf{r}_1 - \mathbf{r}_4) + \delta(\mathbf{r}_2 - \mathbf{r}_4)] f_2^{(\text{eq})}(x_1, x_2) \\
 & \quad + \int dr_3 \int dx_4 C_n(\mathbf{r}_3, \mathbf{r}_4) \delta n(\mathbf{r}_3) (\mathbf{v}_1 \cdot \nabla_1 + \mathbf{v}_4 \cdot \nabla_4 - \bar{T}_{14}) f_2^{(\text{eq})}(x_1, x_4) \\
 & \quad - \int dx_2 \int dr_3 \int dx_4 C_n(\mathbf{r}_3, \mathbf{r}_4) \delta n(\mathbf{r}_3) \bar{T}_{24} \\
 & \quad \times [f_3^{(\text{eq})}(x_1, x_2, x_4) - f_2^{(\text{eq})}(x_1, x_2) f_1^{(\text{eq})}(x_4)] \\
 & = \mathbf{v}_1 \cdot \nabla_1 \int dr_3 \int dx_4 C_n(\mathbf{r}_3, \mathbf{r}_4) \delta n(\mathbf{r}_3) f_2^{(\text{eq})}(x_1, x_4) \\
 & = n_0 f_m(v_1) \mathbf{v}_1 \cdot \nabla_1 \left(\delta n(\mathbf{r}_1) + \int dr_2 C_n(\mathbf{r}_1, \mathbf{r}_2) \delta n(\mathbf{r}_2) \right) \quad (\text{A2.3})
 \end{aligned}$$

where we have used

$$\int d\mathbf{v}_2 f_2^{(\text{eq})}(x_1, x_2) = f_m(v_1) \left(\frac{\delta n(\mathbf{r}_1)}{\delta \lambda(\mathbf{r}_2)} \Big|_{\beta} - n_0 \delta(\mathbf{r}_1 - \mathbf{r}_2) \right) \quad (\text{A2.4})$$

which follows from (3.9).

The other functional derivative can be treated in an analogous manner. Keeping λ constant we have

$$\begin{aligned}
 & \int dx_2 \int dr_3 \bar{T}_{12} \frac{\delta n_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \beta(\mathbf{r}_3)} \Big|_{\lambda} \delta \beta(\mathbf{r}_3) \\
 & = -\frac{1}{2} \int dx_2 \int dx_3 \int dx_4 \delta \beta(\mathbf{r}_3) \varphi(r_{34}) \bar{T}_{12} [f_4^{(\text{eq})}(x_1, x_2, x_3, x_4) \\
 & \quad - f_2(x_1, x_2) f_2(x_3, x_4)] \\
 & \quad - \frac{1}{2} \int dx_2 \int dx_4 [\varphi(r_{14}) \delta \beta(\mathbf{r}_1) + \varphi(r_{24}) \delta \beta(\mathbf{r}_2)] \bar{T}_{12} f_3^{(\text{eq})}(x_1, x_2, x_4) \\
 & \quad - \frac{1}{2} \int dx_2 \int dx_3 [\varphi(r_{13}) \delta \beta(\mathbf{r}_3) + \varphi(r_{23}) \delta \beta(\mathbf{r}_3)] \bar{T}_{12} f_3^{(\text{eq})}(x_1, x_2, x_3) \\
 & \quad - \frac{1}{2} \int dx_2 \varphi(r_{12}) [\delta \beta(\mathbf{r}_1) + \delta \beta(\mathbf{r}_2)] \bar{T}_{12} f_2^{(\text{eq})}(x_1, x_2) \\
 & = \mathbf{v}_1 \cdot \nabla_1 f_m(v_1) \int dr_3 \int dr_4 \delta \beta(\mathbf{r}_3) [\varphi(r_{34})/2] n_3^{(\text{eq})}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4) \\
 & \quad + \mathbf{v}_1 \cdot \nabla_1 f_m(v_1) \int dr_3 [\delta \beta(\mathbf{r}_1) + \delta \beta(\mathbf{r}_3)] [\varphi(r_{13})/2] n_2^{(\text{eq})}(\mathbf{r}_1, \mathbf{r}_3) \\
 & \quad - [\mathbf{v}_1 \cdot \nabla_1 \delta \beta(\mathbf{r}_3)] f_m(v_1) \int dr_3 [\varphi(r_{13})/2] n_2^{(\text{eq})}(\mathbf{r}_1, \mathbf{r}_3) \\
 & \quad + \frac{1}{2} \int dx_2 [\delta \beta(\mathbf{r}_1) + \delta \beta(\mathbf{r}_2)] \\
 & \quad \times [(\bar{T}_{12} - L_0) \varphi(r_{12}) - \varphi(r_{12})(\bar{T}_{12} - I_0)] f_2^{(\text{eq})}(x_1, x_2) \quad (\text{A2.5})
 \end{aligned}$$

by repeatedly using the BBGKY hierarchy equations evaluated in equilibrium. Here L_0 is the free-streaming part of the Liouville operator (see Karkheck *et al* 1985)

$$L_0 = - \sum_i \mathbf{v}_i \cdot \nabla_i. \quad (\text{A2.6})$$

The integrands of the first two terms in (A2.5) can be recognised as

$$\left. \frac{\delta n(\mathbf{r}_1)}{\delta \beta(\mathbf{r}_3)} \right|_{\lambda} \quad (\text{A2.7})$$

and the other terms can be calculated. The final result is

$$\begin{aligned} & \int d\mathbf{x}_2 \int d\mathbf{r}_3 \bar{T}_{12} f_m(v_1) f_m(v_2) \left. \frac{\delta n_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \beta(\mathbf{r}_3)} \right|_{\lambda} \delta \beta(\mathbf{r}_3) \\ &= \mathbf{v}_1 \cdot \nabla_1 f_m(v_1) \left(u_0 \delta \beta(\mathbf{r}_1) + \int d\mathbf{r}_2 \left. \frac{\delta n(\mathbf{r}_1)}{\delta \beta(\mathbf{r}_2)} \right|_{\lambda} \delta \beta(\mathbf{r}_2) \right) \\ &+ n_0^2 (\varepsilon/2) \int d\mathbf{x}_2 f_m(v_1) f_m(v_2) \delta(r_{12} - R) |\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}| g_2(R^-) \\ &\times [\delta \beta(\mathbf{r}_1) + \delta \beta(\mathbf{r}_2)] [\Theta(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} - v_e) - e^{-\beta \varepsilon} \Theta(-\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12})]. \quad (\text{A2.8}) \end{aligned}$$

We now turn to the kinetic equation (4.2) for the potential energy density. Substituting (3.7) and (3.8) into (4.2), performing the velocity integrations and noticing that for $n \geq 2$

$$g_n(\mathbf{r}_1, \mathbf{r}_1 - \hat{\mathbf{r}}_{12} R^+, \dots, \mathbf{r}_n) = e^{-\beta \varepsilon} g_n(\mathbf{r}_1, \mathbf{r}_1 - \hat{\mathbf{r}}_{12} R^-, \dots, \mathbf{r}_n) \quad (\text{A2.9})$$

we find that

$$\begin{aligned} & (\varepsilon/2) \int d\mathbf{v}_1 \int d\mathbf{x}_2 |\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}| [\Theta(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} - v_e) \delta(r_{12} - R^-) \\ & - \Theta(-\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}) \delta(r_{12} - R^+)] \\ & \times f_2^{\text{eq}}(x_1, x_2) \left(\int d\mathbf{r}_3 \left. \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_3)} \right|_{\beta} \delta n(\mathbf{r}_3) + \int d\mathbf{r}_3 \left. \frac{\delta g_2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \beta(\mathbf{r}_3)} \right|_n \delta \beta(\mathbf{r}_3) \right) \\ &= \frac{\varepsilon^2 e^{-\beta \varepsilon} n_0^2 g_2(R^-)}{4(\beta m \pi)^{1/2}} \int d\mathbf{r}_2 \delta(r_{12} - R) [\delta \beta(\mathbf{r}_1) + \delta \beta(\mathbf{r}_2)]. \quad (\text{A2.10}) \end{aligned}$$

Finally we also used the continuity equation,

$$\partial n(\mathbf{r}_1, t) / \partial t = -n_0 \nabla_1 \cdot \int d\mathbf{x}_1 \mathbf{v}_1 f_m(v_1) h(x_1, t) \quad (\text{A2.11})$$

in the derivation of (4.5).

References

- Cohen E G D and de Schepper I M 1987 *J. Stat. Phys.* **46** 949
 Davis H T, Rice S A and Sengers J V 1961 *J. Chem. Phys.* **35** 2210
 de Schepper I, Haffmans A F E M and van Beijeren H 1986 *Phys. Rev. Lett.* **57** 1715

- de Schepper I M, van Rijs J C, Montfrooij W, de Graaf L A, Bruin C and Cohen E G D 1988 *Phys. Rev. A* **38** 271
- Kamgar Parsi B and Cohen E G D 1986 *Physica A* **138** 249
- Karkheck J and Stell G 1981 *J. Chem. Phys.* **75** 1475
- 1983 *J. Phys. Chem.* **87** 2858
- Karkheck J, van Beijeren H, de Schepper I M and Stell G 1985 *Phys. Rev. A* **32** 2517
- Kirkpatrick T R and Nieuwoudt J C 1986 *Phys. Rev. A* **33** 2651
- Konijnendijk H H U and van Leeuwen J M J 1973 *Physica* **64** 342
- Michels J and Trappeniers N 1980 *Physica A* **104** 243
- van Beijeren H and Ernst M H 1973 *Physica* **68** 437; **70** 25
- van Beijeren H, Karkheck J and Sengers J V 1988 *Phys. Rev. A* **37** 2247