# Collective modes in fluids and neutron scattering

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On the basis of a kinetic equation extensions have been obtained for the first time of the five hydrodynamic modes of a dense fluid from the hydrodynamic to the kinetic regime, until they cease to exist. An appreciable softening of the heat mode is found before it becomes a diffusionlike mode. These modes dominate the neutron scattering of fluids.

The scattering of light by a classical fluid in thermal equilibrium is usually discussed on the basis of the hydrodynamic modes which are the eigenvalues and eigenfunctions of the linearized Navier-Stokes equations. Of these five modes only the heat mode and the two sound modes are relevant for the scattering function $S(k,\omega)$. The eigenvalues of these modes are $z_H=-D_Tk^2$ for the heat mode and $z_\pm=\pm ick-\Gamma k^2$ for the sound modes, with $D_T$ the thermal diffusivity, $c$ the sound velocity, and $\Gamma$ the sound absorption of the fluid. The heat mode leads to a central or Rayleigh line in $S(k,\omega)$ with a height $\sim z_H^{-1}$ and a half-width $\sim z_H$, while the sound modes lead to Brillouin lines at $\pm ick$, with heights $\sim(\Gamma k^2)^{-1}$ and half-widths $\sim\Gamma k^2$.

The scattering of neutrons, on the other hand, is usually treated on the basis of either generalized hydrodynamics using memory kernels, or kinetic theory using the Boltzmann or an Enskog type equation.[1,2] In particular, Furtado *et al.*[3] have discussed neutron scattering using the generalized Enskog equation for a dense fluid of hard spheres that has been derived by many authors.[4] In order to compute the coherent and incoherent neutron-scattering functions $S(k,\omega)$ and $S_s(k,\omega)$ and compare these with experiment, Furtado *et al.* approximate the collision operator occurring in the Enskog equation and in addition assume a wave-vector-($k$-) dependent hard-sphere diameter. Here we also start from the generalized Enskog equation but approximate the collision operator only. For explicit results one needs the mass $m$ and the diameter $\sigma$ of the particles, the number density $n$, the temperature $T(\beta=1/k_BT)$, and the theoretical equilibrium radial distribution function $g(r)$ of a hard-sphere system.[5] It is shown that for dense fluids the Navier-Stokes equations can be used for reduced wave vectors $k\sigma\lesssim 1$, and that for $1\lesssim k\sigma\lesssim 30$, the continuations of the hydrodynamic modes still describe the main features of $S(k,\omega)$ and $S_s(k,\omega)$.

$S(k,\omega)$ and $S_s(k,\omega)$ of a hard-sphere fluid are, according to the generalized Enskog theory,[2]

$$S(k,\omega)=\frac{1}{\pi}S(k)\,\mathrm{Re}\left\langle\frac{1}{i\omega-L_{\vec{k}}}\right\rangle, \qquad (1)$$

$$S_s(k,\omega)=\frac{1}{\pi}\,\mathrm{Re}\left\langle\frac{1}{i\omega-L_{\vec{k}}^D}\right\rangle, \qquad (2)$$

where $\langle\cdots\rangle=\int d\vec{v}\phi(v)\cdots$, with $\phi(v)$ the normalized Maxwell velocity distribution function, $\vec{v}$ the velocity of a fluid particle, and $S(k)$ the static structure factor. The generalized Enskog operator $L_{\vec{k}}$ is

$$L_{\vec{k}}=-i\vec{k}\cdot\vec{v}+n\chi\Lambda_{\vec{k}}+nA_{\vec{k}}. \qquad (3)$$

Here $i\vec{k}\cdot\vec{v}$ is the "free-streaming" part, $\chi=g(\sigma)$, $\Lambda_{\vec{k}}$ a binary collision operator

$$\Lambda_{\vec{k}}h(\vec{v})=\sigma^2\int d\hat{\sigma}\int d\vec{v}'\phi(v')\Theta(\Delta\vec{v}\cdot\hat{\sigma})\Delta\vec{v}\cdot\hat{\sigma}\times\{h(\vec{v})-h(\vec{v}^*)+e^{-i\vec{k}\cdot\hat{\sigma}\sigma}[h(\vec{v}')-h(\vec{v}'^*)]\}, \qquad (4)$$

where $\hat{\sigma}$ is a unit vector, $\Theta(x)$ the unit step function, $\Delta\vec{v}=\vec{v}-\vec{v}'$, $\vec{v}^*=\vec{v}-\Delta\vec{v}\cdot\hat{\sigma}\hat{\sigma}$, and $\vec{v}'^*=\vec{v}'+\Delta\vec{v}\cdot\hat{\sigma}\hat{\sigma}$. $\Lambda_0$ is the linearized Boltzmann collision operator. The "mean-field" operator $A_{\vec{k}}$ in (3) is

$$A_{\vec{k}}h(\vec{v})=D(k)\int d\vec{v}'\phi(v')i\vec{k}\cdot\vec{v}'h(\vec{v}'), \qquad (5)$$

where $D(k)=C(k)-\chi C_0(k)$, $nC(k)=1-1/S(k)$, and $C_0(k)$ is the low-density limit of $C(k)$, the direct correlation function. We note that

$$\lim_{k\to 0}A_{\vec{k}}=\lim_{k\to\infty}A_{\vec{k}}=0.$$

In (2), $L_{\vec{k}}^D=-i\vec{k}\cdot\vec{v}+n\chi\Lambda^D$, where $\Lambda^D=\lim_{k\to\infty}\Lambda_{\vec{k}}$, the Lorentz-Boltzmann operator. To calculate $S(k,\omega)$ and $S_s(k,\omega)$ explicitly, we approximated $\Lambda_{\vec{k}}$ in (3) in a Bhatnagar-Gross-Krook (BGK)-type fashion.[2,6,7] Thereto averages $\langle\,\rangle$ are considered to be innerproducts in a Hilbert space of functions of $\vec{v}$. One introduces a complete set of orthonormal polynomials in $\vec{v}$, $\{\varphi_i\}$, that transforms $\Lambda_{\vec{k}}$ into an infinite matrix operator. The approximation consists in taking into account exactly a finite part of this matrix, while the remaining part is represented by a few matrix elements only. We have used the following approximate expression $\Lambda_{\vec{k}}^{(M)}$ for $\Lambda_{\vec{k}}$, which is analogous to, but different from that of Furtado *et al.*:

$$\Lambda_{\vec{k}}^{(M)} = \sum_{i,j=1}^{M} |\varphi_i > f_{ij}(k) < \varphi_j| + [g_+(k)\varphi_2 + h_+(k)P_\perp]P_+ + [g_-(k)\varphi_2 + h_-(k)P_\perp]P_- . \quad (6)$$

The number $M$ and the polynomials $\varphi_1, \ldots, \varphi_M$ are given below, $P_\perp$ projects orthogonal to $\varphi_1, \ldots, \varphi_M$, $P_+$ projects onto functions of $\vec{v}$ that are even in $v_x$ and $v_y$ (with $\vec{k}$ in the $z$ direction), $P_- = 1 - P_+$. The $M^2+4$ functions $f_{ij}$, $g_\pm$, $h_\pm$ are determined by the requirements that $\Lambda_{\vec{k}}^{(M)}$ reproduces exactly the $M\times M$ part of the $\Lambda_{\vec{k}}$ matrix with respect to $\varphi_1, \ldots, \varphi_M$ and two diagonal and two off-diagonal elements outside the $M\times M$ block, for which two more polynomials are given below.

We note that (a) for $k=0$ and $\infty$ (6) represents the usual BGK approximations for $\Lambda_0$ and $\Lambda^D$, respectively. (b) Using $L_{\vec{k}}^{(M)}$ for $L_{\vec{k}}$ (i.e., $\Lambda_{\vec{k}}$ replaced by $\Lambda_{\vec{k}}^{(M)}$) and $L_{\vec{k}}^{D(M)}$ for $L_{\vec{k}}^{D}$ ($\Lambda^D$ replaced by $\Lambda_\infty^{(M)}$), $S(k,\omega)$ and $S_s(k,\omega)$ can be calculated explicitly.[3] (c) The eigenvalues ($z_i(k)$, $z_i^D(k)$) and eigenfunctions ($\psi_i(k,\vec{v})$, $\psi_i^D(k,\vec{v})$) of $L_{\vec{k}}^{(M)}$ and $L_{\vec{k}}^{D(M)}$ are obtained using the inverse-Laplace-transform method.[6,7] (d) The contribution of the heat mode alone, $S^{(H)}(k,\omega)$ to $S(k,\omega)$, is

$$S^{(H)}(k,\omega) = \frac{1}{\pi} S(k) \mathrm{Re} \frac{M_H(k)}{i\omega - z_H(k)}, \quad (7)$$

where $M_H(k) = \langle\psi_H(k,\vec{v})\rangle\langle\Phi_H(k,\vec{v})\rangle$ with $\Phi_H$ the left eigenfunction of $L_{\vec{k}}^{(M)}$ that corresponds to the right eigenfunction $\psi_H$, (e) The contribution of the diffusion mode alone, $S_s^{(D)}(k,\omega)$ to $S_s(k,\omega)$, is given by an expression similar to (7) with $S(k)$ replaced by 1, $z_H(k)$ by $z_D(k)$, and $M_H(k)$ by $M_D(k)$.

We have carried out explicit calculations on the basis of Eq. (6) with $M=5$, and $f_{ij}$, $g_\pm$, and $h_\pm$ determined by $\langle\varphi_i\Lambda_{\vec{k}}^{(M)}\varphi_j\rangle = \langle\varphi_i\Lambda_{\vec{k}}\varphi_j\rangle$ with $i,j=1,\ldots,5$, $i=j=6$, $i=j=7$, $i=3$, $j=7$, $i=4$, $j=6$, and $\varphi_1, \ldots, \varphi_7$ proportional to 1, $v_z$, $\beta m\vec{v}^2-3$, $v_x$, $v_y$, $v_xv_z$, and $v_z(\beta m\vec{v}^2-5)$, respectively, i.e., the five conserved quantities of $\Lambda_0$, a momentum flux and a heat flux.

The eigenvalues $z_i(k)$ of $L_{\vec{k}}^{(M)}$ are plotted in Fig. 1 as a function of $k\sigma$ for a typical liquid density. The validity of the Navier-Stokes expressions, $-D_Tk^2$ for the heat mode and $\pm ick - \Gamma k^2$ for the sound modes, is restricted to wave vectors $k\sigma \lesssim 1$. While the sound modes show considerable structure for $k\sigma \gtrsim 1$ [both $z_+(k)$ and $z_-(k)$ are real for $5.7 \lesssim k\sigma \lesssim 7.4$], they have the characteristics of strongly damped kinetic modes up to $k\sigma \simeq 10$ where they cease to exist. The heat mode softens for $k\sigma \gtrsim 1$, almost vanishes at $k\sigma \simeq 7$, and then oscillates around the diffusion mode. It ceases to exist at $k\sigma \simeq 30$, very much beyond the sound modes. The cutoff wave vectors are of the order of the inverse mean free path $l^{-1}$ ($l^{-1} = \pi\sqrt{2}\chi n\sigma^2 = 19.32\,\sigma^{-1}$) just as at low densities.[7]

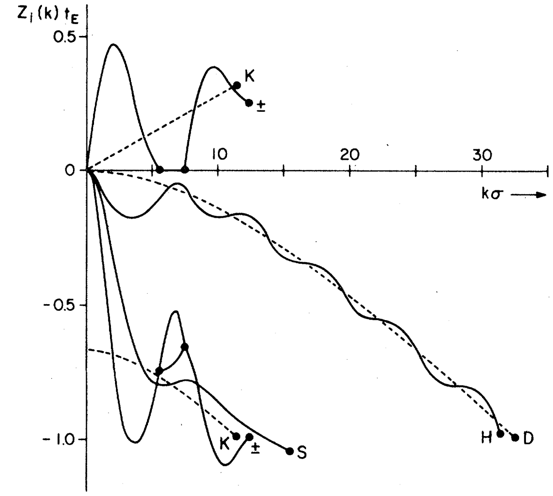


FIG. 1. Eigenvalues $z_i$ of $L_{\vec{k}}$ (drawn lines) and $L_{\vec{k}}^{D}$ (dotted lines) as functions of $k\sigma$ for a hard-sphere fluid at density $n\sigma^3 = 0.884$, $t_E = l/\langle v\rangle$. $i$ stands for heat ($H$), sound ($\pm$), shear ($S$), diffusion ($D$) and kinetic ($K$) modes. Positive values refer to imaginary parts, negative values to real parts.

The eigenvalues $z_i^D(k)$ of $L_{\vec{k}}^{D(M)}$ are also plotted in Fig. 1. Except for the diffusion mode there are two strongly damped kinetic modes. The diffusion mode continues smoothly beyond the Navier-Stokes regime where $z_D(k) = -Dk^2$, with $D$ the self-diffusion constant, until it ceases to exist at $k\sigma \simeq 30$. Deviations of $z_D(k)$ from $-Dk^2$ grow as large as 30% for $k\sigma \simeq 30$. Since $L_{\vec{k}}$ approaches $L_{\vec{k}}^{D}$ for large $k$, $S(k,\omega)$ approaches $S_s(k,\omega)$ and the eigenvalues of $L_{\vec{k}}$ approach those of $L_{\vec{k}}^{D}$: the heat mode to the diffusion mode and the two sound modes to the two kinetic modes of $L_{\vec{k}}^{D}$.

This behavior of the extended hydrodynamic modes leads, for a hard-sphere fluid, to the following consequences for $S(k,\omega)$ and $S_s(k,\omega)$:

(1) $S(k,\omega=0)$ as well as the half-width $\omega_h(k)$, defined by $S(k,\omega_h) = \frac{1}{2}S(k,0)$, exhibit pronounced oscillatory behavior as functions of $k\sigma$ (cf. Figs. 2 and 3). This behavior is directly related to that of $S^{(H)}(k,\omega)$, for the relative difference of $S^{(H)}(k,0)$ and $S(k,0)$ and that between $\omega_h(k)$ and $-z_H(k)$ is only a few percent for $0 \lesssim k\sigma \lesssim 20$ and not larger that 20% even for $k\sigma \simeq 30$. Since $M_H(k)$ in (7) varies

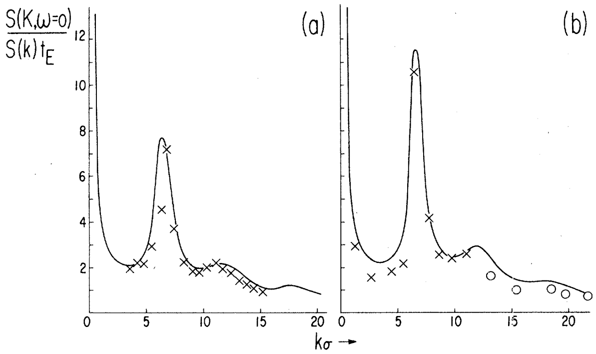


FIG. 2. $S)k,0)/S(k)t_E$ as a function of $k\sigma$ at $n\sigma^3=0.884$ (a) and 0.923 (b) for hard spheres (drawn lines) and liquid argon ($x$) (a) and liquid rubidium ($x$, 0) (b). For argon $\sigma=3.46$ Å, $t_E=0.084$ ps, for rubidium $\sigma=4.44$ Å and $t_E=0.070$ ps. For rubidium, $x$ and 0 refer to experiments with different incident neutron energies (Ref. 9). Drawn lines are indistinguishable from $S^{(H)}(k,0)/S(k)t_E$.

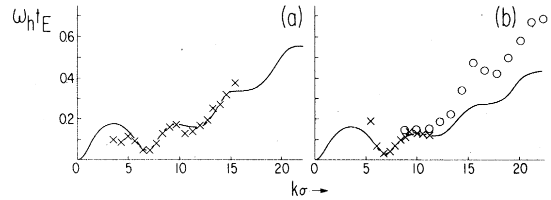


FIG. 3. Half-width at half-height $\omega_h$ of $S(k,\omega)$ as function of $k\sigma$ for hard spheres (drawn lines) and liquid argon ($x$) (a) and liquid rubidium ($x$, 0) (b). $\sigma$, $n\sigma^3$, and $t_E$ are as in Fig. 2. Drawn lines are indistinguishable from $-z_H(k)t_E$.

smoothly between 0.63 and 1.7 for $0 \lesssim k\sigma \lesssim 30$, the structure of $S(k,0)/S(k) \sim z_H(k)^{-1}$ and $\omega_h(k) \sim z_H(k)$ is mainly determined by $z_H(k)$. Thus the central line in $S(k,\omega)$ around $\omega=0$ is dominated by the contribution of the heat mode and can be considered as a Rayleigh line.

(2) The sound modes manifest themselves as visible Brillouin lines in $S(k,\omega)$ only for $0 \lesssim k\sigma \lesssim 0.5$

(3) $S_s(k,\omega)$ is given by $S_s^{(D)}(k,\omega)$ within the same accuracy as $S(k,\omega)$ was given by $S^{(H)}(k,\omega)$. Since $M_D(k)$ varies monotonically from 1 to 1.7 for $0 \lesssim k\sigma \lesssim 30$, $S_s^{(D)}(k,\omega)$ is mainly determined by $z_D(k)$.

In Figs. 2 and 3 we compare the hard-sphere prediction for $S(k,0)$ and $\omega_h(k)$ with those obtained from neutron-scattering experiments in liquid argon[8] and liquid rubidium.[9] Thereto the hard-sphere diameter $\sigma$ was determined as the average of those values of $\sigma$ for which the locations and the heights of the first two maxima of $S(k)$ coincide with the corresponding quantities for hard spheres, respectively. Owing to the good agreement in Figs. 2 and 3, we believe also that in real liquids the extended heat mode dominates the central line of $S(k,\omega)$.

For liquid argon, Brillouin lines in $S(k,\omega)$ are visible until $k\sigma \simeq 1$,[1] for liquid rubidium until $k\sigma \simeq 4$,[9] and for hard spheres until $k\sigma \simeq 0.5$. Thus, while the existence of sound modes in the neutron-scattering regime is a general feature, their visibility in $S(k,w)$ depends on the nature of the fluid. For instance, using Navier-Stokes hydrodynamics for argon, rubidium, and hard spheres up to $k\sigma \simeq 1$, differences in $S(k,\omega)$ can be accounted for by differences in thermodynamic and transport properties, the pronounced Brillouin lines of rubidium arising from an abnormally large $D_T$.

It has been noticed for liquid argon[8] that $S_s(k,\omega)$ is approximately represented by $\pi^{-1}\mathrm{Re}[1/(i\omega+Dk^2)]$ for all $k\sigma \lesssim 16$. On the basis of our theory we would rather expect $S_s(k,\omega)$ to be represented by $S_s^{(D)}(k,\omega)$. Present experiments agree with both representations.

Thus it appears that not only can collective excitations be defined in dense fluids for $k\sigma \simeq 30$ (or wavelengths $\lambda \gtrsim \frac{1}{5}\sigma$), the behavior of $S(k,\omega)$ and $S_s(k,\omega)$ is dominated by these modes for all $k$ for which they exist.

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