Half Width of Neutron Spectra

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We analyzed for the first time systematically the half widths of a great variety of neutron spectra of simple dense classical fluids as functions of wave number and density. We find that the observed behavior of the half width near its minimum value can be understood quantitatively on the basis of a generalization of a diffusion model, proposed before.

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Since the work of de Gennes[1] it has been noted that the normalized second frequency moment $\omega_0(k)$ of the dynamical structure factor $S(k,\omega)$ of the coherent neutron spectra of simple dense fluids has a sharp minimum at values of the wave number k such that $k\sigma \simeq 2\pi$, where σ characterizes the size of the fluid particles. This follows immediately from the exact expression for $\omega_0(k)$,

$$\omega_0(k) = [\langle\omega^2\rangle/\langle\omega^0\rangle]^{1/2} = k[\beta m S(k)]^{-1/2}. \quad (1)$$

Here $\langle\omega^n\rangle = \int_{-\infty}^{+\infty} d\omega\, \omega^n S(k,\omega)$ is the nth frequency moment of $S(k,\omega)$, $\beta = 1/k_B T$, where k_B is Boltzmann's constant, T the temperature of the fluid, m the mass of a fluid particle, and $\langle\omega^0\rangle = S(k)$ the static structure factor, which has a sharp maximum near $k\sigma = 2\pi$. This maximum in $S(k)$ causes a minimum in $\omega_0(k)$ which, for a Gaussian $S(k,\omega)$, implies a minimum of the half width at half height $\omega_H(k)$ of $S(k,\omega)$, since for a Gaussian $S(k,\omega)$ $\omega_H(k) = 1.18\omega_0(k)$.

In addition, as was particularly emphasized by Egelstaff,[2] the observed deviation of $\langle\omega^4\rangle$ from its Gaussian value of $3\langle\omega^2\rangle^2/\langle\omega^0\rangle$ implies a further sharpening of $S(k,\omega)$ that leads to an additional reduction of the linewidth near $k\sigma \approx 2\pi$. Moreover, it has been noted that the oscillations in $\omega_0(k)$ are roughly in phase with the oscillations in the half width at half height $\omega_H(k)$,[2,3] so that, in general, a minimum in $\omega_0(k)$ is indicative of a minimum in $\omega_H(k)$. This similarity between $\omega_0(k)$ and $\omega_H(k)$ is only qualitative, however.[2]

A physical picture for the behavior of $\omega_H(k)$ was proposed many years ago by Egelstaff[2] and Sköld.[4] These authors associated $\omega_H(k)$ with the inverse lifetime of a nonpropagating diffusive mode of the fluid. In this Letter we show quantitatively that for sufficiently high densities, $\omega_H(k)$ can indeed be interpreted, in the region of its minimum near $k\sigma = 2\pi$, in terms of an inverse relaxation time, which is related to the very slow structural relaxation of a density fluctuation in a dense fluid via a self-diffusion process.

We consider experimental data for $\omega_H(k)$ as a function of wave number and density for a variety of simple fluids (krypton,[5] argon,[6-9] neon,[10] and rubidium[11]), as well as for model fluids consisting of Lennard-Jones[12,13] or hard-sphere particles.[14,15]

In Figs. 1(a)-1(e), the reduced half width at half height $\omega_H t_\sigma$ as well as $\omega_0 t_\sigma$ are represented as functions of the reduced wave number $k\sigma$ for dense Kr, Ar, and Rb under a number of different conditions, where the characteristic time $t_\sigma = (\beta m)^{1/2}\sigma/2$ in all cases. We note the following:

(a) In Fig. 1 we have ordered the neutron-scattering data with respect to increasing reduced density $V_0/V = n\sigma^3/\sqrt{2}$. Here V_0 is the volume V at close packing of an equivalent hard-sphere fluid, where the hard-sphere diameter σ is determined by the condition that the first peak in $S(k)$ of the equivalent hard-sphere fluid and the corresponding real fluid coincide. $V_0/V = 0.45$, 0.53, 0.58, 0.625, and 0.653 in Figs. 1(a)-1(e), respectively.

(b) Although the thermodynamic states of Kr and Ar in Fig. 1(a) correspond to each other,[5,7] considerable deviations between their neutron spectra are found which are not understood at present. However, their observed values for $\omega_H t_\sigma$ [cf. Fig. 1(a)] and $\omega_0 t_\sigma$ are identical for $k\sigma$ in the neighborhood of the de Gennes minimum in $\omega_0(k)$, the region of interest to us here.

(c) The data for $\omega_H t_\sigma$ and $\omega_0 t_\sigma$ of Ar displayed in Fig. 1(b) are, for all k, indistinguishable from those of neon[10] and those of a Lennard-Jones fluid[13] at corresponding thermodynamic states.

(d) Molecular-dynamics data for $\omega_H t_\sigma$ and $\omega_0 t_\sigma$ of hard-sphere fluids at the reduced densities $V_0/V = 0.58$ (Ref. 14) and $V_0/V = 0.625$ (Ref. 15) agree well with the $\omega_H t_\sigma$ and $\omega_0 t_\sigma$ displayed in Figs. 1(c) and 1(d), respectively, in particular in the neighborhood of the de Gennes minimum.[16]

(e) One observes in Fig. 1, in agreement with earlier observations by Egelstaff on liquid Ar, that $\omega_0(k)$

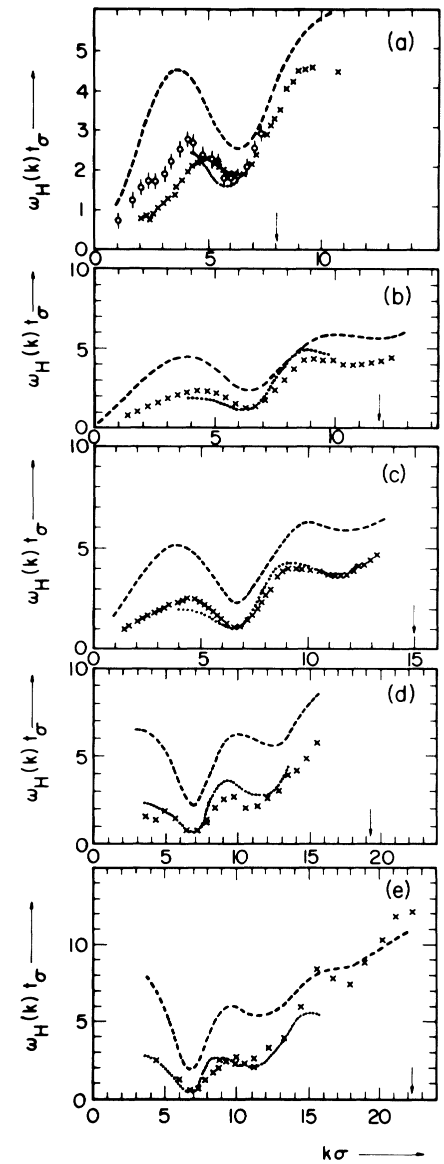

FIG. 1. Reduced half widths $\omega_H(k)t_\sigma$ as functions of $k\sigma$. (a) Crosses, Kr at $T=297$ K and $n=13.84$ nm^{-3} ($\sigma=0.359$ nm, $t_\sigma=1.05$ ps) (Ref. 5); circles, Ar at $T=212$ K and $n=17.0$ nm^{-3} ($\sigma=0.334$ nm, $t_\sigma=0.77$ ps) (Ref. 9). (b) Ar at $T=120$ K and $n=18.5$ nm^{-3} ($\sigma=0.343$ nm, $t_\sigma=1.03$ ps) (Ref. 7). (c) Ar at $T=120$ K and $n=20.1$ nm^{-3} ($\sigma=0.343$ nm, $t_\sigma=1.03$ ps) (Ref. 7). (d) Ar at $T=86$ K and $n=21.3$ nm^{-3} ($\sigma=0.346$ nm, $t_\sigma=1.30$ ps) (Ref. 6). (e) Rb at $T=315$ K and $n=10.6$ nm^{-3} ($\sigma=0.443$ nm, $t_\sigma=1.27$ ps) (Ref. 11). Also shown are the reduced $\omega_0(k)t_\sigma$ (dashed line) [cf. Eq. (1)] and the theoretical $\omega_H(k)t_\sigma$ (dotted line) [cf. Eq. (2)]. The vertical arrows point to the values of $k\sigma$ where $k=l^{-1}$, an upper bound for the wave number for which Eq. (2) is valid for $\omega_H(k)$. Note the minima at $k=k^*$ near $k\sigma=2\pi$.

$\geq \omega_H(k)$ and that the ratio $\omega_0(k)/\omega_H(k)$, which increases for $4\leq k\sigma\leq 10$ with increasing density, strongly depends on k, at fixed density. This is particularly striking in Fig. 1(e), where $\omega_0(k)/\omega_H(k)\simeq 1$ for $k\sigma\simeq 20$ and $\omega_0(k)/\omega_H(k)\simeq 4$ for $k\sigma$ near the de Gennes minimum.

Since $\omega_H(k)$ is related to intermediate values of ω in $S(k,\omega)$, it refers to physical processes on an intermediate time scale. In fact, for the dense fluids and the k values considered here, it is a self-diffusion-like process of the particles in the fluid that enables a density fluctuation to relax. This process is well known in the theory of structural relaxation of dense fluids.[17–20]

Although no theoretical expression for $\omega_H(k)$ is available for real fluids like Ar or Ne, or for model Lennard-Jones fluids, such an expression has been derived, albeit approximately, for a dense hard-sphere fluid. This formula for $\omega_H(k)$ in the neighborhood of the de Gennes minimum reads[13,20]

$$\omega_H(k)=[D_E k^2/S(k)]d(k), \tag{2a}$$

where, in very good approximation,

$$d(k)=[1-j_0(k\sigma)+2j_2(k\sigma)]^{-1}. \tag{2b}$$

Here D_E is the self-diffusion coefficient of the hard-sphere fluid in the Enskog theory[21] and $j_0(x)$ and $j_2(x)$ are the zeroth- and second-order spherical Bessel functions, respectively. For a plot of $d(k)$ and $S(k)$ we refer to Ref. 13. Equation (2) only holds for high densities and intermediate values of k: $1<k\sigma<\sigma/l$, where $\sigma/l\gg 1$. For in the derivation of Eq. (2) the conservation laws for the local microscopic velocity and energy have not been taken into account. Since these are relevant only for density fluctuations with wavelength $\lambda=2\pi/k$ much larger than σ, Eq. (2) applies when $k\sigma>1$. In addition, since self-diffusion-like behavior obtains for density fluctuations only when their wavelength λ is much larger than the mean free path between collisions l, Eq. (2) applies when $kl<1$.

In Fig. 1 we compare in detail the theoretical $\omega_H(k)$ as computed from Eq. (2) for an equivalent hard-sphere fluid with the experimental values for $\omega_H(k)$, as a function of k. One notes that for the region where Eq. (2) applies, the experimental $\omega_H(k)$ are far better described by the theoretical $\omega_H(k)$ than by $\omega_0(k)$, in particular at the higher densities and $k\sigma$ near 2π.

A similar comparison can be made for $\omega_H(k)$ as a function of the density n. $\omega_H(k)$, as given by Eq. (2), depends on n via $D_E/S(k)$. Although $D_E/S(k)$ is a quantity that refers to an equivalent hard-sphere fluid, one would expect that its density dependence reflects the dramatic increase in difficulty of fluid particles to diffuse past each other in a dense fluid, when the density increases. This is borne out in Fig. 2. Here the experimental values $\omega_H(k^*)$ of $\omega_H(k)$ at $k=k^*$, where the minimum of $\omega_H(k)$ occurs, are plotted, which strongly decrease with increasing density. In addition, this decrease is very well described by the minimum values $\omega_H(k^*)$ of the theoretical $\omega_H(k)$ of Eq. (2). One also

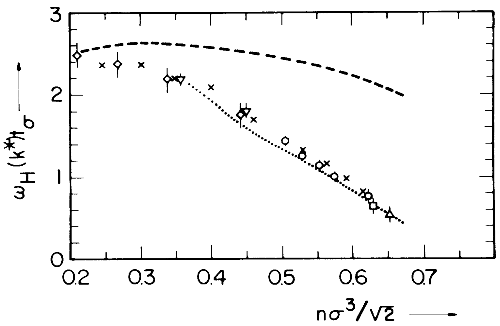

FIG. 2. Lozenges, density dependence of $\omega_H(k^*)t_\sigma$ for Ar at 212 K (Ref. 9); inverted triangle, Kr at 297 K (Ref. 5); circles, Ar at 120 K (Refs. 7 and 8); squares, Ar at 86 K (Ref. 6); triangles, Rb at 315 K (Ref. 11); and crosses, a Lennard-Jones fluid at $k_BT/\epsilon_{LJ}=1.71$ ($\sigma=0.981\sigma_{LJ}$) (Ref. 22). Also shown are the density dependences of $\omega_0(k^*)t_\sigma$ (dashed line) [cf. Eq. (1)] and the theoretical $\omega_H(k^*)t_\sigma$ (dotted line) [cf. Eq. (2)].

sees in Fig. 2 that $\omega_0(k^*)$ shows only a very weak density dependence which is markedly different from that of $\omega_H(k^*)$. The experimental results for $\omega_H(k^*)$ represented in Fig. 2 are those given in Refs. 5–9 and 11 for Kr, Ar, and Rb, as well as these of recent molecular-dynamics simulations for a Lennard-Jones fluid at nine different densities,[22] at the reduced temperature $k_BT/\epsilon_{LJ}=1.71$, where ϵ_{LJ} is the Lennard-Jones potential well depth. We conclude from Figs. 1 and 2 that for dense Kr, Ar, Ne, Rb, and Lennard-Jones and hard-sphere fluids,[13,16] the behavior of $\omega_H(k)$ with $k\sigma$ near 2π can be understood on the basis of Eq. (2), i.e., a self-diffusion process.

We end with two remarks:

(1) The expression (2) for $\omega_H(k)$ of the half width of $S(k,\omega)$ of a dense hard-sphere fluid in the neutron-scattering regime is analogous to that of a dilute colloidal solution of polystyrene spheres in the light-scattering regime. This has been discussed elsewhere.[23]

(2) Equation (2) describes the density behavior of $\omega_H(k^*)$ as long as $k^* < l^{-1}$, i.e., for reduced densities down to $V_0/V \simeq 0.35$ (cf. Fig. 2), where $k^* \simeq 2\pi/\sigma \approx l^{-1}$. We see in Fig. 2 that for $V_0/V < 0.35$, the experimental $\omega_H(k^*)$ show a tendency to approach $\omega_0(k^*)$, i.e., towards ideal-gas-like behavior. This might suggest a continuation of the experimental points in Fig. 2 with decreasing density through the $\omega_0(k)$ curve towards the ideal-gas limit of $1.18\omega_0(k)$ at very low densities.

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