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Comment on "Collective modes in fluids and neutron scattering"

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de Schepper and Cohen have shown recently that the hydrodynamic modes for a hard-sphere fluid may be extended to quite large wave vectors, and that at high densities the hydrodynamic part of the dynamical-structure factors dominates over a wide range of wave vectors. The objective here is to describe the results of a similar analysis of two simple models of the self-structure factor. The simplicity of the models allows a scaling of the frequency and wave vectors such that a universal form independent of potential model, density, and temperature is obtained. The diffusion mode and hydrodynamic part of the self-structure factor are calculated, leading to a behavior similar to that observed by de Schepper and Cohen.

I. INTRODUCTION

In a recent calculation,[1] de Schepper and Cohen showed, on the basis of a kinetic model for the hard-sphere Enskog equation, that the hydrodynamic modes exist in a dense fluid even for wavelengths smaller than the hard-sphere diameter. Furthermore, the contribution of such extended hydrodynamic modes provides the dominant part of the dynamic-structure factor, $S(k,\omega)$, and the self-structure factor, $S_s(k,\omega)$. The purpose of this comment is to clarify the results of Ref. 1 for two models of $S_s(k,\omega)$ that are sufficiently simple that the analytic structure can be studied in some detail. Each model admits a scaling such that $S_s(k,\omega)$ may be written in a universal form independent of the potential model and thermodynamic state parameters. The results may therefore be considered as suggestive of the properties of fluids in general, rather than anomalies of the hard-sphere fluid. The first model is a single relaxation-time equation where the relaxation time is characterized by the self-diffusion constant; the second model is the Fokker-Planck (FP) equation. Both equations are exactly solvable and each describes hydrodynamic modes as well as more complex microscopic excitations. The hydrodynamic modes and hydrodynamic parts of $S_s(k,\omega)$ are then easily calculated, as well as $S_s(k,\omega)$ itself for comparison.

The self-structure factor may be expressed in terms of an average of the solution to a formally exact linear kinetic equation with the result[2]

$$S_s(k,\omega)=2\,\mathrm{Re}[1,R(k,\omega)1]\ , \tag{1}$$

$$R\equiv[-i\omega+i\vec{k}\cdot\vec{v}+\hat{M}(k,\omega)]^{-1}\ . \tag{2}$$

Here $\hat{M}(k,\omega)$ is the formal collision operator characterizing the kinetic equation. $\vec{v}$ is the velocity of the tagged particle and the scalar product is defined by

$$(a,b)\equiv\int d\vec{v}\,f_0(v)a^*(\vec{v})b(\vec{v})\ . \tag{3}$$

Finally, $f_0(v)$ is the Maxwell-Boltzmann distribution, and Re in Eq. (1) denotes the real part.

Evaluation of the scalar product in Eq. (1) for a given operator, $\hat{M}(k,\omega)$, is, in general, prohibitively difficult. In practice $\hat{M}$ is replaced by a kinetic model operator whose properties exactly reproduce those of $\hat{M}(k,\omega)$ considered most important. Since 1 is an eigenfunction of $\hat{M}(k,\omega)$ with zero eigenvalue, a commonly used and reasonably accurate kinetic model is[2,3]

$$\hat{M}(k,\omega)\to M(k,\omega)(1-P)\ , \tag{4}$$

where P is the projection operator onto 1 and $M(k,\omega)$ is the function

$$M(k,\omega)\equiv[\vec{v},\hat{M}(k,\omega)\vec{v}]/(\vec{v},\vec{v})\ . \tag{5}$$

With this choice a dimensionless form for $S_s(k,\omega)$ is easily found to be

$$R(x,y)\equiv kv_0S_s(k,\omega)=2\,\mathrm{Re}\frac{\phi(z)}{i-yM^*(x,y)\phi(z)}\ , \tag{6}$$

where $\phi(z)$ is the plasma dispersion function,[4] and,

$$z=x+iyM^*(x,y)\ ,$$

$$x\equiv\frac{\omega}{kv_0}\ ,\quad y\equiv\frac{M_0}{kv_0}=\frac{v_0}{2Dk}\ . \tag{7}$$

The constant v_0 is the thermal velocity, $v_0 \equiv (2k_BT/m)^{1/2}$, $M_0 \equiv M(0,0)$ is the low-frequency, low wave-vector limit of $M(k,\omega)$ and D is the coefficient of self-diffusion. Also $M^*(x,y) \equiv M(k,\omega)/M(0,0)$. The dependence of $M(k,\omega)$ on k and ω is due to spatial variations of the particles during collisions and to the finite duration of a collision. This dependence is therefore expected to be important only for $\omega\sigma/v_0 > 1$ and $k\sigma > 1$, where σ is the force range. In terms of the variables x and y, this gives $\omega\sigma/v_0 \sim n^*x/y$ and $k\sigma \sim n^*/y$, where $n^* \equiv n\sigma^3$, and n is the density. The range of values of x of interest in determining the half-width of the structure factor is $0 \leq x \lesssim 1$. Furthermore, as shown in the next section, the extension of the hydrodynamic diffusion mode exists only if $y \gtrsim 0.5$, for this model. At low density, for the x and y values considered $M^*(x,y) \approx M^*(0,0) = 1$. For moderate density and very small values of y, M^* might change appreciably even in the range $0 \leq x \lesssim 1$. However, only the combination yM^* appears in Eq. (6), so that the approximation $M^* \approx 1$ is reasonable over a wide range of densities for the values of x and y considered.[5] In this case Eq. (6) becomes

$$R(x,y) = 2\,\mathrm{Re}\frac{\phi(x+iy)}{i - y\phi(x+iy)}\ , \tag{8}$$

and the self-structure factor has a universal form depending on the potential model only through the definition of y. Equation (8) will be referred to as the single relaxation-time model.

The second model considered here is obtained by choosing for $\hat{M}(k,\omega)$ the linearized Fokker-Planck operator. The approximation of Eq. (4) is not required since $R(x,y)$ can be calculated exactly.[6] The result is

$$R_{\mathrm{FP}}(x,y) = 2\,\mathrm{Re}\int_0^\infty dt\, e^{ixt}\exp\left[-\frac{t}{2y} + \frac{1}{2y^2}(1 - e^{-yt})\right]\ , \tag{9}$$

where x and y are the same parameters as in Eq. (7). It may seem that the Fokker-Planck equation is not an appropriate model for $S_s(k,\omega)$ since it is generally justified only for the motion of a large particle in a fluid. However, the same result would be obtained from the less restrictive assumptions that the time correlation function determining $S_s(k,\omega)$ is Gaussian in k, and that the velocity autocorrelation function decays exponentially in time. These assumptions are indeed qualitatively correct for simple fluids.

II. RESULTS

The extent to which hydrodynamic modes exist in the fluid and constitute the dominant part of $S_s(k,\omega)$ may be investigated by examining the analytic structure of $R(x,y)$ for the two models considered. The hydrodynamic part of the self-structure factor is written in terms of a single nonpropagating mode,

$$R^H(x,y) = 2\,\mathrm{Re}\frac{A(y)}{-ix + D(y)}\ , \tag{10}$$

such that $D(y)$ vanishes for large y. This form reproduces the entire $R(x,y)$ for large y when the self-structure factor is the solution of a diffusion equation and $A(y) \rightarrow 1$, $D(y) \rightarrow 1/2y$.

First the model given by Eq. (8) is considered. The hydrodynamic part of $R(x,y)$ may be extracted by searching for the pole $x_0(y) = -iD(y)$ which goes to the diffusion limit, $-i/2y$, for large values of y. The pole is therefore expected to be pure imaginary and is given by the solution of the equation

$$i - y\phi[x_0(y) + iy] = 0\ . \tag{11}$$

Equation (11) has been solved using tabulated values of the plasma dispersion function.[4] A solution with the correct asymptotic limit exists only for $y \geq [\mathrm{Im}\phi(i0)]^{-1} \sim 0.57$. (At the reduced density $n^* = 0.884$ used in Ref. 1 this value corresponds to $k\sigma \sim 22.6$.) At the smallest values of y for which the hydrodynamic solution exists, deviations of $D(y)$ from $1/2y$ are as large as 30%. In Fig. 1 the half-width of $R^H(x,y)$ is compared with the half-width of $R(x,y)$ as given by Eq. (8). As observed by de Schepper and Cohen, most of the self-structure factor is given by $R^H(x,y)$ for values of $y \geq 1$. Significant deviations start appearing for $y < 1$.

Next consider the Fokker-Planck, or Gaussian, model of Eq. (9). The hydrodynamic part may be identified by expanding $\exp[-(1/2y^2)e^{-yt}]$ and evaluating the integral to give

$$R_{\rm FP}(x,y)=2\,{\rm Re}\,e^{1/2y^2}\sum_{q=0}^{\infty}\frac{1}{q!}\left[\frac{1}{2y^2}\right]^q\left[-ix+\frac{1}{2y}+qy\right]^{-1}\,. \qquad (12)$$

The spectrum consists of an infinite number of equally spaced simple poles along the negative imaginary axis, and the hydrodynamic mode is identified as that of the $q=0$ pole. For this model the hydrodynamic pole has the same form for all y, $x_0(y)=-i/2y$, and exists for all y. The hydrodynamic part is

$$R^H(x,y)=\frac{e^{1/2y^2}}{y}[x^2+(1/2y)^2]^{-1}\,. \qquad (13)$$

Figure 2 shows a comparison of the half-width of the hydrodynamic part with that for the complete series. Again, the hydrodynamic part dominates over the region $y>1$.

III. DISCUSSION

The range of frequencies and wave vectors, ω and k, for which hydrodynamics fails is referred to as the kinetic regime. It is readily shown that for arbitrary y there are significant deviations from the hydrodynamic value at sufficiently large x. This corresponds to times short compared to the collision frequency, and typically occurs far out in the wings of $S_s(k,\omega)$ or $R(x,y)$ for a moderately dense fluid. In contrast, for values of x less than or of the order of the half-width $(0\leq x \lesssim 1)$ the calculations of Sec. II show that the hydrodynamic range corresponds to $y\gtrsim 1$.

To clarify why the hydrodynamic part dominates for $y\gtrsim 1$, note that the spectrum of $R(x,y)$ is qualitatively expected to consist of a hydrodynamic pole nearest the origin and microscopic singularities (continuous or discrete) starting at the collision frequency. In terms of the variables x and y the collision frequency is proportional to y. Consider a simple example consisting of only two simple poles,

$$R(x,y)=2\,{\rm Re}\left[\frac{A_H(y)}{-ix+p_H(y)}+\frac{A_m(y)}{-ix+p_m(y)}\right], \qquad (14)$$

where $p_H(y)$ and $p_m(y)$ are the hydrodynamic and microscopic poles, respectively, and $A_H(y)$ and $A_m(y)$ are the residues of these poles. Then, since the peak of $R(x,y)$ is centered at $x=0$, the pole nearest the origin will dominate unless the residue of the microscopic pole is larger than that of the hydrodynamic pole. This possibility is excluded by the first two frequency moments of $S_s(k,\omega)$ which imply $A_H+A_m=1$ and $p_HA_H+p_mA_m=0$. Then Eq. (14) may be written

$$R(x,y)=2\,{\rm Re}\frac{1}{(p_m-p_H)}\times\left[\frac{p_m}{-ix+p_H}-\frac{p_H}{-ix+p_m}\right]. \qquad (15)$$

Clearly, the hydrodynamic part will dominante whenever $p_H(y)<p_m(y)$. Also, this inequality is

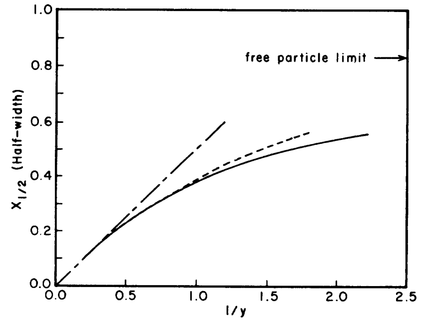

FIG. 1. Half-width at half maximum of $R(x,y)$ given by Eq. (8) for the single relaxation-time model (——), and half-width for the hydrodynamic part only (— — —); also shown is the asymptotic form, $1/2y$, for the hydrodynamic part (-----).

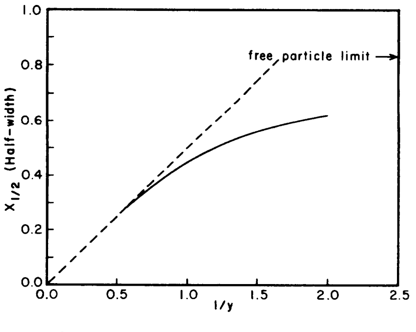

FIG. 2. Half-width at half maximum for $R_{\rm FP}(x,y)$ given by Eq. (12) for the Fokker-Planck or Gaussian model (——), and for the hydrodynamic part (— — —).

the condition one would expect for the existence of hydrodynamics (i.e., that it is the slowest decaying mode of the fluid), so quite generally it may be expected that the hydrodynamic part of $R(x,y)$ should dominate over the entire range of y for which the hydrodynamic mode exists. To estimate this range, $p_H(y)\sim 1/2y$ and $p_m(y)\sim y$, so that $p_H(y)=p_m(y)$ at about $y=1$, as found in Sec. II.

These features of the simple two-pole model in Eq. (15) are easily verified for the Fokker-Planck or Gaussian model. The analytic structure of the single relaxation-time model is considerably more complex because of the branch cuts in the plasma dispersion function, $\phi(z)$. Since the hydrodynamic mode is also more complex in this case it may appear that the discussion based on Eq. (15) might not apply. However, there is a simple and reasonably accurate approximation for $\phi(z)$ given by[7]

$$\phi(z)\sim\frac{|a|^2}{2a_R}\left[\frac{1}{a(a-z)}-\frac{1}{a^*(a^*+z)}\right], \qquad (16)$$

where the real and imaginary parts of a are determined by the large z expansion of $\phi(z)$. Use of Eq. (16) in Eq. (8) leads to a two-pole representation for $R(x,y)$. Repeating the calculations of Sec. II gives the results shown in Fig. 3. Although some quantitative differences between Fig. 1 and 3 are noticeable, the qualitative features are clearly preserved by the two-pole representation.

The parameter y is a measure of the ratio of the wavelength, $\lambda\equiv 2\pi/k$, to the mean-free path, $l\equiv v_0\tau_c$. If the collision time is taken to be the relaxation time for the velocity autocorrelation function, $\tau_c=2D/v_0^2$, then $y=\lambda/2\pi l$. The limit for the applicability of hydrodynamics, $y=1$, corresponds to wavelengths of the order of or smaller than the mean-free path. At low or moderate densities, the mean-free path is large compared to atomic dimensions and it is perhaps not too surprising that hydrodynamics is applicable even at wavelengths close to the mean-free path. However, at liquid densities the mean-free path can be comparable to, or smaller than, the atomic dimensions. Consequently the condition $y=1$ corresponds to wavelengths also of the order of atomic dimensions. (For the condition of reference 1 this is $\lambda\sim 0.3\sigma$, where σ is the hard-shape diameter.) This is a considerably more interesting result, although some caution is required since neither the Enskog model of Ref. 1, nor those discussed here are reliable at such high densities.[8]

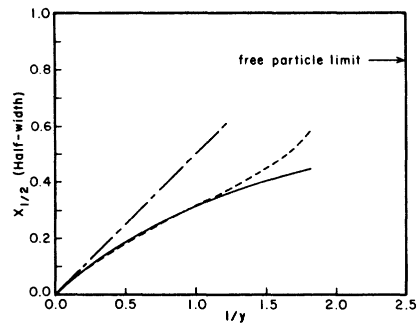

FIG. 3. Same as Fig. 1, except with the two-pole approximation, Eq. (16).

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