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Short-wavelength collective modes and generalized hydrodynamic equations for hard-sphere particles

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The extended hydrodynamic modes recently discussed by de Schepper, Cohen, and collaborators using an approximate hard-sphere kinetic equation are computed here with use of approximate hard-sphere generalized hydrodynamic equations. The theory presented here is completely analytic and reproduces the results of de Schepper *et al.* for dense hard-sphere fluids reasonably well. The connection to previous theories based on generalized hydrodynamics is discussed.

In some recent papers de Schepper[1–3] and co-workers discussed short-wavelength collective modes in hard-sphere fluids. They used the revised Enskog kinetic equation to calculate the extension of the usual hydrodynamic modes to large wave numbers k. These authors showed that not only do collective modes exist at large wave numbers, but in dense hard-sphere fluids the neutron scattering structure factor $S(k,\omega)$, with ω the frequency, can be quantitatively represented for $0<k\sigma<15$, with σ the molecular diameter, as a superposition of three extended hydrodynamic modes, a heat mode, and two sound modes. They therefore concluded that $S(k,\omega)$ for neutron scattering is a simple extension of $S(k,\omega)$ for light scattering.

Related work has been done by Alley, Alder, and Yip.[4] They used computer molecular dynamics for hard-sphere fluids to determine the wave-number-dependent transport coefficients that should be used in hard-sphere generalized hydrodynamic equations.

In this Comment I establish the connection between the kinetic theory results of de Schepper *et al.*, the results of Alley *et al.*, and the method of generalized hydrodynamics.[5] In particular, I show here how the results of de Schepper and co-workers can be understood with use of a simple but approximate set of generalized hydrodynamic equations.

The basic idea is as follows. First, note that the revised Enskog equation used by de Schepper *et al.* is exact for hard spheres at short times.[6] Its use for longer times is *ad hoc* but qualitatively correct. Even at short times all of the important excluded volume correlations in the hard-sphere fluid are present. The proposal here is to use a similar short-time approximation at the level of generalized hydrodynamics. That is, a short-time approximation is used to evaluate explicitly the wave-number- and frequency-dependent transport coefficients that appear in generalized hydrodynamics. It will be argued below that this is a reasonable procedure for dense hard-sphere fluids.

To proceed I use the standard projection operator[5] method to derive generalized hydrodynamic equations for the equilibrium time correlation functions in a hard-sphere fluid. The method is identical to that given elsewhere, except the time dependence is generated by the pseudo-Liouville operator for hard-sphere particles.[7] The resulting equations contain a frequency-independent $\underline{\Omega}$ matrix and a frequency-dependent memory kernel.[5] In the short-time approximation used here the memory kernel vanishes. The net result is a closed set of generalized hydrodynamic equations for the time correlation functions of mass density ρ, longitudinal momentum density l, temperature T, and transverse momentum density t_i $(i=1,2)$. Denoting normalized time correlation functions in Fourier-Laplace (z) space by $G_{\alpha\beta}(k,z)$, $\alpha,\beta=\rho,l,T,t_i$ the equations of motion are

$$zG_{\rho\beta}(k,z)-\frac{ik}{\sqrt{\beta mS(k)}}G_{l\beta}(k,z)=\delta_{\rho\beta}\ , \tag{1a}$$

$$zG_{l\beta}(k,z)-\frac{ik}{\sqrt{\beta mS(k)}}G_{\rho\beta}(k,z)-ik\left[\frac{2}{3\beta m}\right]^{1/2}\left[1+2\pi n\sigma^3\chi(\sigma)\frac{j_1(k\sigma)}{k\sigma}\right]G_{T\beta}(k,z)+\frac{2}{3t_E}[1-j_0(k\sigma)+2j_2(k\sigma)]G_{l\beta}(k,z)=\delta_{l\beta}\ , \tag{1b}$$

$$zG_{T\beta}(k,z)-ik\left[\frac{2}{3\beta m}\right]^{1/2}\left[1+2\pi n\sigma^3\chi(\sigma)\frac{j_1(k\sigma)}{k\sigma}\right]G_{l\beta}(k,z)+\frac{2}{3t_E}[1-j_0(k\sigma)]G_{T\beta}(k,z)=\delta_{T\beta}\ , \tag{1c}$$

and $(i=1,2)$,

$$\left[z+\frac{2}{3t_E}[1-j_0(k\sigma)-j_2(k\sigma)]\right]G_{t_i\beta}(k,z)=\delta_{t_i\beta} \ . \quad \text{(1d)}$$

Here $j_l(k\sigma)$ is the spherical Bessel function of order l, n is the number density, m is the mass, $\beta=(k_BT)^{-1}$, with T the temperature, $\chi(\sigma)$ is the radial distribution function at contact, $S(k)$ is the static structure faction, and $t_E=\sqrt{\beta m\pi}/4\pi n\sigma^2\chi(\sigma)$ is the Enskog mean free time between collisions.[1–4] It should be remarked that Eqs. (1) can also be obtained from the results of Alley and Alder,[4] if only the collisional contributions to the transport coefficients are retained in their generalized hydrodynamic equations.

Examining Eqs. (1), we next discuss their validity. In the limit of small k, Eqs. (1) reduce to the usual linearized hydrodynamic equations for hard spheres with the exact thermodynamic coefficients. The transport coefficients are given by their Enskog values if one retains only the collisional contributions.[4,8] Physically, this is expected, since it is these contributions that are instantaneous in hard-sphere systems and hence survive in the instantaneous limit. We conclude that Eqs. (1) are reasonable only for dense hard-sphere fluids, since it is only for dense fluids that the collisional contributions represent important contributions to transport. Further, it is reasonable to think that these equations are even more realistic as k and z increase. This is supported by the results of Alley *et al.*[4] These authors used computer molecular dynamics to establish that for intermediate values of k the k-dependent transport coefficients are well approximated by their collisional contributions.

The generalized hydrodynamic equations given by Eqs. (1) define an eigenvalue problem that can be solved analytically. I will use the terminology shear, heat, and sound modes to identify the five hydrodynamic modes for large k, in order to maintain continuity in k. The solution involves a cubic equation, since Eqs. (1a)–(1c) are coupled together. Explicit results for the extended hydrodynamic eigenvalues are given in Fig. 1 for a reduced density $n\sigma^3=0.88$ ($v_0/v=0.625$, with v_0 the volume of close packing and v the volume per particle) and for $0<k\sigma<10$. I used the Percus-Yevick representation (with an approximate Verlet-Weiss correction) for $S(k)$.[9] From these results the hydrodynamic eigenfunctions can be explicitly determined. As an example, the quantity $A_H^2(k)=M_H(k)$ calculated by de Schepper and Cohen[1] is given in Fig. 2. $M_H(k)$ essentially determines the amplitude of $S(k,\omega)$ for neutron scattering from dense hard-sphere fluids. These results will be discussed in more detail below.

A standard approximation made when discussing effects on the molecular length scale is to neglect temperature variations or fluctuations.[5,10] In view of the results given above, where the heat mode was shown to exhibit a dramatic softening near $k\sigma\approx 6.8$, one might think that the most important physical effect was being neglected. To show that this reasoning is not correct, I have solved Eqs. (1) neglecting terms involving temperature fluctuations, $G_{T\beta}(k,z)$. There are then only four hydrodynamic modes with the two shear modes not affected by this approximation. The remaining two modes are sound modes for small k and the explicit expression for their associated eigenvalues can be easily determined from Eqs. (1a) and (1b), neglecting $G_{T\beta}(k,z)$. These two eigenvalues are graphed, for $n\sigma^3=0.88$, in Fig. 3.

The propagation gap becomes considerably larger than the full solution illustrated in Fig. 1. In the propagation gap one of the sound modes, $z_+(k)$, is very strongly damped, while the other, $z_-(k)$, softens appreciably. In Fig. 4, we graph $z_-(k)$ in the gap, $z_H(k)$ from the complete solution, as

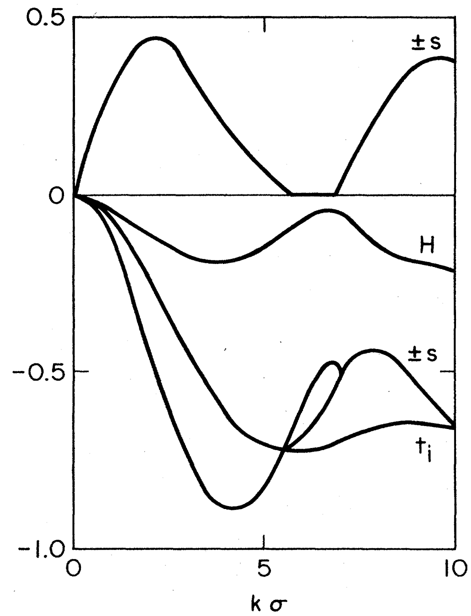

FIG. 1. Eigenvalues $z_i(k)$ of Eqs. (1) as functions of $k\sigma$ for a hard-sphere fluid at a density $n\sigma^3=0.88$, typical for liquids. i stands for heat (H), shear (t_i), and sound ($\pm s$) modes. Positive value refers to the absolute value of the imaginary parts of $z_i(k)$ and negative values refer to real parts.

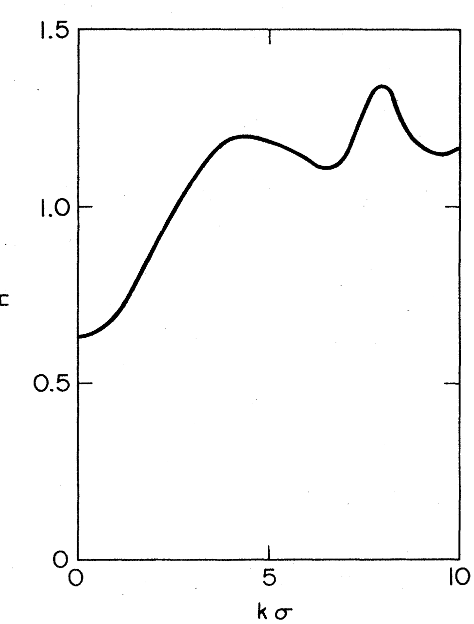

FIG. 2. A_H^2 as a function of $k\sigma$ for hard spheres at density $n\sigma^3=0.88$.

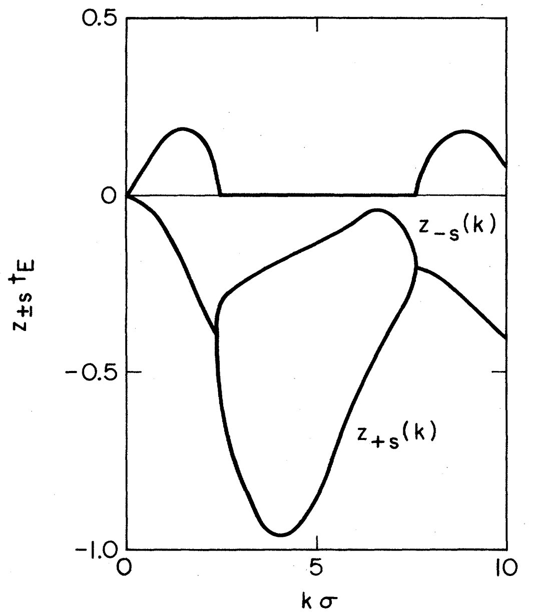

FIG. 3. Extended sound eigenvalues as functions of $k\sigma$ when temperature fluctuations are neglected. The fluid density is $n\sigma^3=0.88$ and the notation is as in Fig. 1.

well as an approximation for $z_H(k)$, for k not too small, that follows from the revised Enskog kinetic equation,[2,11]

$$z_H(k) = -\frac{Dk^2}{S(k)}[1-j_0(k\sigma)+2j_2(k\sigma)]^{-1} \ . \qquad (2)$$

Here $D=3t_E/2\beta m$ is the Enskog self-diffusion coefficient. For a range of k values these eigenvalues are all essentially identical. This implies that for a range of k values, temperature fluctuations can be neglected and the most important aspect of the extended hydrodynamic modes, the softening of the heat modes, is still effectively present. Physically this is because for these values of k the heat mode in the complete solution is mainly determined by number density and longitudinal momentum density fluctuations.

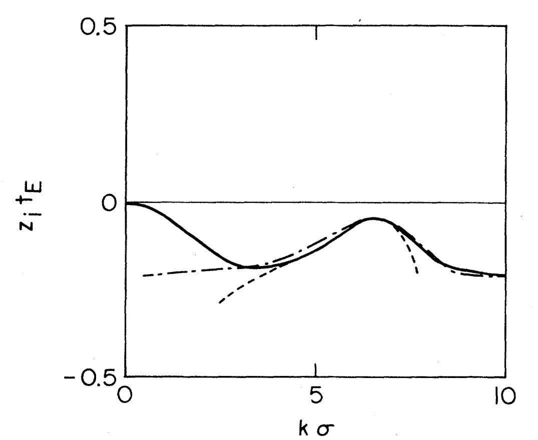

FIG. 4. Comparison between the extended heat mode of Eqs. (1) (——); approximation for this mode for k not too small, given by Eq. (2) (— · — ·); and the soft approximate extended sound mode in Fig. 3 (— — —). The hard-sphere fluid density here is $n\sigma^3=0.88$.

This Comment is concluded with a few remarks.

(1) Clearly, the most important aspect of these results, illustrated in Fig. 1, is the softening of the heat mode near $k\sigma\approx 6.8$. It is due to both the peak in $S(k)$ near $k\sigma\approx 6.8$ and the fact that the heat mode has become essentially a density mode which decays via self-diffusion [cf. Eq. (2)] on these length scales. It should be noted that to obtain these results both k-dependent thermodynamics as well as k-dependent transport coefficients are needed. This softening leads to a very slow relaxation time for dynamical processes taking place on a molecular length scale. This slow mode can be used as an input to theories which include mode coupling effects. Such theories have been used to understand qualitatively the anomalous long-time tails[11-13] and shear-dependent viscosity[14,15] observed in computer simulations. Furthermore, a theory for the glass transition observed in computer simulations of simple liquids has recently been developed based on the softening of the heat mode.[16] In the language used here, this soft mode is also the cause of the de Gennes minimum observed in neutron scattering.[1] The results for the extended heat mode given here are in quantitative agreement with those of de Schepper *et al.*, except near $k=0$.

It is tempting to interpret the softening of the heat mode as being due to slow structural relaxation in a dense fluid, although other interpretations are possible.[4] One can interpret the minimum value of $|z_H(k)|$ for k not small as being present due to an elementary rate process by which structure can relax. Furthermore, for $k\sigma\gtrsim 6.8$ the k dependence of this slow mode is essentially given by the self-diffusion hydrodynamic mode.[1] This is the other process by which structure can relax. One then obtains a physical picture essentially equivalent to that used by Montrose and Litovitz[17] in their phenomenological treatment of structural relaxation in very dense liquids. In the language of kinetic theory this mode for $k\sigma\gtrsim 6.8$ acts very much like a slowly decaying kinetic mode.

(2) The results for the extended sound modes given in Fig. 1 are also in good agreement with the recent results of Zuilhof, Cohen, and de Schepper[2] except near $k\sigma\cong 8$, where our results show a smaller damping. Related to this is that $A_H^2(k)$ given in Fig. 2 is slightly larger near $k\sigma\cong 8$ than the kinetic theory results previously reported.[1]

Zuilhof *et al.*[2] have interpreted the presence of a propagation gap as being due to a competition between elasticity and dissipation. The structure of the theory presented here confirms this picture. The disappearance of propagating modes in a dense fluid at large wave numbers is certainly not surprising physically; it is easy to imagine an effective pinning or trapping of a sound wave on a molecular scale. The reappearance of the propagating modes for larger k is somewhat more surprising. Physically, it is similar to the depinning of sound waves in a porous medium at large frequencies, where the effective viscosity or damping becomes smaller.[18]

(3) de Schepper, Van Rijs, and Cohen[19] have recently pointed out that the usual small wave-number Navier-Stokes equations also exhibit a propagation gap if these equations are assumed to be valid for large wave numbers. They have studied in detail the conditions needed for the gap to appear by adjusting the phenomenological parameters

in the hydrodynamic equations.

(4) The shear or viscous mode eigenvalues in Fig. 1 are also in qualitative agreement with the results of de Schepper, Cohen, and Zuilhof[1,2] for $k\sigma \lesssim 10$. It is interesting to note that propagating shear modes in dense hard-sphere fluids at large k are not predicted by the theory presented here, although they are observed[4,20] in computer simulations of dense hard-sphere fluids. Further, distinct shear waves are not a consequence of the revised Enskog kinetic equation.[1,4] It appears,[11,21] at least for hard-sphere systems, that mode coupling effects are needed to account theoretically for the shear waves observed in computer simulations. Here it should be noted that these mode coupling calculations are not the usual ones, where only long-wavelength effects are taken into account. They also take into account effects on a molecular scale. The important physical point is that the softening of the heat mode on a molecular scale introduces a slow relaxation time into the discussion of dynamical processes in a dense fluid. In the formalism used in this paper these mode coupling effects were neglected when the short-time approximation for the memory kernel was used.

(5) With the results given here, the dynamic structure factor $S(k,\omega)$ can be easily computed. Explicit results will not be given here, since we would essentially reproduce the results of de Schepper *et al.*[1,2] It is worthwhile remarking, however, that for most values of k the dominant contribution is simply the extended heat mode. This follows not only because this mode is the slowest relaxing mode, but also because its amplitude is much larger than that of the sound modes. It is also interesting to note that for intermediate values of k, the amplitude of one of the extended sound mode's contribution to $S(k,\omega)$ is negative. Physically this is not a cause for concern, since for these wave numbers the modes are not separated and the total $S(k,\omega)$ is still positive.[2]

(6) Previous experimental workers have concluded that propagating short-wavelength collective modes do not exist in simple classical liquids.[22] This seems to be in conflict with the results reported here and elsewhere. To understand that it is not, we first note that the propagating modes discussed here are very strongly damped at large k and hence are not true collective modes. Secondly, the lack of distinct side peaks in neutron or Raman scattering experiments does not imply the absence of propagating modes. It only implies that if they exist they are sufficiently broad that the side peaks overlap with the central line.[2]

(7) In using a short-time approximation to obtain Eqs. (1), we have effectively retained only what is usually denoted as the $\underline{\Omega}$ matrix in the generalized hydrodynamic literature.[5] For continuous potentials this matrix does not contain dissipative terms. For hard spheres this is not the case. It is a subtle problem to take the hard-sphere limit of the usual generalized hydrodynamic equations for continuous potentials. Here this technical problem is avoided by considering hard-sphere particles from the very beginning.

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