Dynamic Structure Factor of a Helium-Neon Dense Gas Mixture: Crossover from Hydrodynamics to the Microscopic Regime

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The dynamic structure factor for a dense gas He/Ne mixture is calculated by molecular dynamics. At length scales within the realm of hydrodynamics, $k \leq 0.03$ Å^{-1}, the spectrum shows a well-resolved Rayleigh-Brillouin triplet, evidencing the presence of sound-wave excitations. For intermediate wave vectors, the partial spectra apart from showing a broadening of the inelastic peaks unveil the presence of two additional modes with phase velocities below and above hydrodynamic sound. The present results cover a broad range of wave vectors, which cannot, at present, be reached by experimental techniques, and where present theoretical approaches are not well established.

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The spectrum of the light scattered (LS) by a fluid composed of a binary mixture is well understood on linearized hydrodynamics grounds [1], and the line shape of the inelastic peaks can be adequately accounted for by shifted Lorentzians with frequencies $\omega_s(k) = \pm c_s k$, where c_s is the adiabatic sound velocity, being such predictions in good agreement with extensive LS work on dense rare gas mixtures [2]. The interest in such simple systems was reawakened by theoretical results based upon the revised Enskog theory (RET) regarding mixtures of hard spheres with disparate masses. In fact, as predicted by Campa and Cohen [3], two propagating kinetic modes (i.e., different from hydrodynamic sound), one of them exhibiting a phase velocity higher than that corresponding to a continuation to larger wave vectors of hydrodynamic sound, called "fast sound" hereinafter, were found for moderate densities. There, sound propagation was found to involve density fluctuations of both components, whereas the fast sound only involved those regarding the light component which take place on the background of the heavy particles [3]. The origin of the second kinetic mode which evidenced phase velocities below the sonic ones was somewhat unclear [4], although it was later identified with the propagation of density fluctuations of the heavy component and thus named "slow sound" [5]. As proofs demonstrating the existence of fast sound, computer simulation results of the alloy $Li_{0.8}Pb_{0.2}$ [6] and dense He/Ne mixtures [7,8] were brought forward. However, system-size limitations precluded the exploration of wave vectors small enough to reach full hydrodynamic behavior. In particular, it was unclear at that time [3,5] whether both kinetic modes merged with the hydrodynamic excitation at low k [9], or even the extent of departures from hydrodynamic, linear dispersion, to be expected for the normal sound mode at intermediate wave vectors. On experimental grounds, the dynamic structure factor of He/Ne mixtures was measured by neutron scattering (NS) [8,9], and the spectra analyzed assuming the existence of the fast and slow kinetic modes (i.e., two shifted Lorentzians), thus leading to fair agreement with RET predictions [3]. It was predicted that the slow mode should merge with hydrodynamics at $k < k_h$, with $k_h = 0.07$ Å^{-1}, whereas the fast mode vanishes in such a limit [9]. Recently, it has also been predicted from a two-temperature model that dilute mixtures can show a propagation gap on the sound mode, depending upon the composition of the mixture, so that sound excitations can go continuously into the fast or slow kinetic modes at large enough wave vectors [10].

We have previously shown how molecular dynamics (MD) simulation can bridge the gap between hydrodynamic and microscopic domains, thus allowing the exploration of a kinematic region unreachable by present LS and NS techniques [11]. The purpose of this Letter is thus to provide simulational evidence regarding a model He/Ne mixture, at length and time scales covering a range where departures from hydrodynamics start to be noticeable. Because of the slow decay of concentration fluctuations, the statistical uncertainties due to the time window of our simulation preempt any straight analysis of the quasielastic peak of the spectra, whereas a quantitative analysis of the damping and dispersion of the sound and kinetic modes can be carried [11] on safe grounds. The present results thus unveil the nature of the crossover to the hydrodynamic limit in the He/Ne mixture, and clarify the role of both components as far as normal sound propagation is concerned as well as the origin of the two kinetic modes at intermediate k values, which are related to the decoupled motions of the two components.

We have modeled such a mixture by enclosing 4154 He atoms and 1030 Ne atoms, hereinafter also denoted by components 1 and 2, respectively, in a rectangular parallelepiped of sides $930.84 \times 19.39 \times 19.39$ Å with periodic boundary conditions [11]. The particles interact

through Lennard-Jones (LJ) potentials with parameters $\epsilon/k(\mathrm{He}) = 10$ K, $\sigma(\mathrm{He}) = 2.602$ Å, $\epsilon/k(\mathrm{Ne}) = 42$ K, $\sigma(\mathrm{Ne}) = 2.755$ Å, and Lorentz-Berthelot rules for the cross interactions. The integration of the equations of motion was performed in the microcanonical ensemble (NVE) using the leap-frog algorithm and time steps $\delta t = 0.005\,24$ ps. The thermodynamic state under consideration corresponds to $T = 39.3$ K and particle number density $n = 0.0151$ Å^{-3} [5,7], which is close enough to that analyzed within the RET approach [8,9]. For reducing statistical uncertainties we have performed nine independent runs of an average length of 2 ns each. During the simulation run the Fourier components of the microscopic partial number densities along the larger side of the simulation box with a time increment $60\delta t$ were evaluated and kept for later analysis.

The normalized total dynamic structure factor $S(k,\omega)$ measured in neutron scattering experiments is given in terms of the partial functions $S_{ij}(k,\omega)$ by

$$S(k,\omega) = x_1 b_1^2 S_{11}(k,\omega) + x_2 b_2^2 S_{22}(k,\omega) + 2(x_1 x_2)^{1/2} b_1 b_2 S_{12}(k,\omega), \quad (1)$$

where $b_i^* = b_i/(x_1 b_1^2 + x_2 b_2^2)^{1/2}$, with b_i being the scattering length of the components (natural abundances, $b_{\mathrm{He}} = 3.26$ fm and $b_{\mathrm{Ne}} = 4.55$ fm) and x_i the molar fraction of the components. The $S_{ij}(k,\omega)$ are given by

$$S_{ij}(\mathbf{k},\omega) = \frac{1}{2\pi(N_i N_j)^{1/2}} \int dt\, e^{i\omega t} \langle \delta n_i^*(\mathbf{k},0)\delta n_j(\mathbf{k},t)\rangle, \quad (2)$$

where N_s is the particle number of the species s and $\delta n_s(\mathbf{k},t)$ is a density fluctuation of wave vector $\mathbf{k}$, i.e., $\delta n_s(\mathbf{k},t) = \sum e^{i\mathbf{k}\cdot\mathbf{r}_s^{(p)}(t)}$ and $\mathbf{r}_s^{(p)}(t)$ the position of particle p of species s at time t. The angular brackets of Eq. (2) denote the equilibrium canonical ensemble average, and the star denotes complex conjugation.

The results for the $S(k,\omega)$ of the mixture measurable by neutron scattering techniques are shown in Fig. 1 as function of ω for different wave vectors with a resolution of 0.0025 ps^{-1}. For $k = 0.0276$ Å^{-1}, the Rayleigh-Brillouin (RB) spectrum is well defined, indicating the hydrodynamic behavior of the mixture. The maximum of the Brillouin peak occurs at $\omega_s(k) = c_s k$, with $c_s = 3.7$ Å ps^{-1} obtained from the extrapolated limit of the total structure factor $S(0) = 0.84$, and from the heat capacities ratio obtained from Monte Carlo (NPT and NVT) simulations, which gives $\gamma = 2.5$, and the average molecular weight is $M = x_1 M_1 + x_2 M_2$. The value for c_s is close to that predicted from the van der Waals equation $= 3.83$ Å ps^{-1} [8]. The sound damping estimated from the $\Gamma(k)$ widths of the spectra for $k \leq 0.055$ Å^{-1} follows a k^2 behavior, with a coefficient of 20 Å^2 ps^{-1}, that is about twice the Enskog prediction of 10.7 Å^2 ps^{-1} [8]. For $k = 0.11$ Å^{-1}, $S(k,\omega)$ shows a broad propagative mode, see Fig. 1(b), which is basically constituted of the strongly damped sonic and emergent kinetic modes together with the long tails of the nonpropagating contributions. The intensity of the sound mode is still dominant and the location of the maximum follows the hydrodynamic prescription. In Fig. 2 we show the partial $S_{ij}(\mathbf{k},\omega)$ at $k = 0.082$ Å^{-1}. The maximum of the propagative mode supported by He atoms still follows the hydrodynamics prescription, but the partials for the Ne contributions show the maximum at slightly

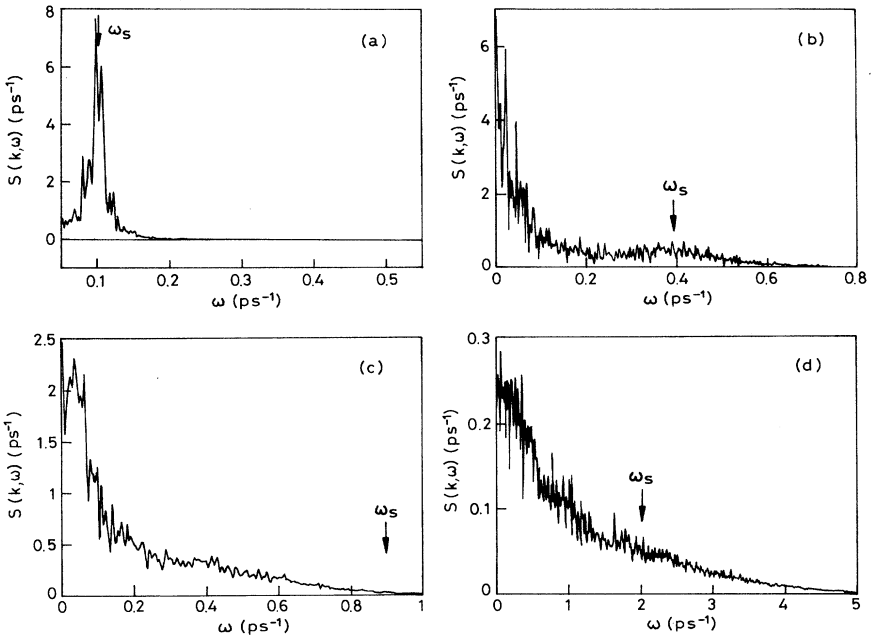

FIG. 1. $S(k,\omega)$ for different wave vectors: (a) $k = 0.0276$ Å^{-1}, (b) $k = 0.11$ Å^{-1}, (c) $k = 0.25$ Å^{-1}, and (d) $k = 0.54$ Å^{-1}. ω_s denotes the hydrodynamics predicted location of the sound mode in the spectra.

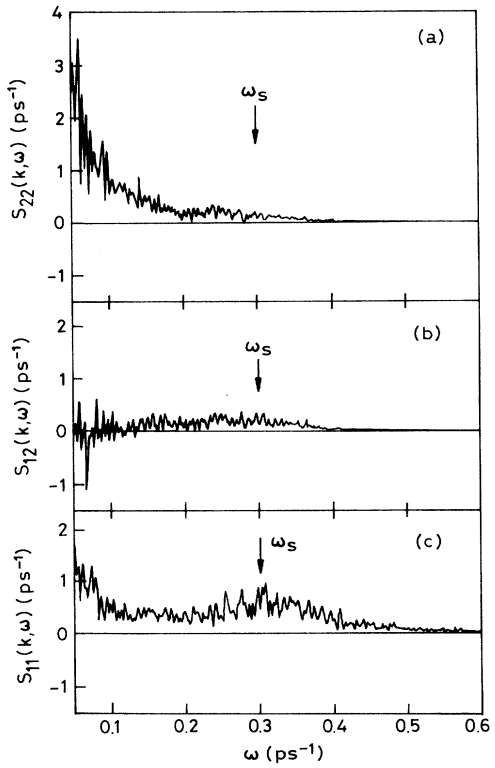

FIG. 2. Partial $S_{ij}(k,\omega)$ 1 = He, 2 = Ne structure factors for $k = 0.082$ Å^{-1}: (a) $S_{22}(k,\omega)$, (b) $S_{12}(k,\omega)$, and (c) $S_{22}(k,\omega)$

lower frequencies. The region $0.05 < k < 0.2$ Å^{-1} is associated with the crossover from hydrodynamics to kinetic regimes of the system. At low wave vectors $S(k,\omega)$ shows a broad dispersive mode at high frequencies which arises from sonic and kinetic contributions, the former mode disappearing at large wave vectors of such interval, Fig. 1(c). At the highest wave vectors the reduction of the intensity of the Rayleigh peak of $S_{ij}(k,\omega)$ unveils the presence of different shoulders which can be originated by the remanent propagative modes of the system.

To quantify the dispersion of different modes, the spectra of the partial longitudinal currents $J_{ij}(k,w) \propto C_{ij}(k,\omega) = \omega^2 S_{ij}(k,\omega)$ are introduced and two of them shown in Fig. 3. Notice that because of the large damping the frequencies corresponding to the maxima of $C_{ij}(k,\omega)$ will be larger than those of the maxima of the Brillouin peaks, and, in fact, the former ones can be written as $\Omega_c(k) = \sqrt{\omega_s(k)^2 + \Gamma(k)^2}$, that is, the bare ω_s frequencies are dressed by the damping terms [12]. In terms of the partials, the broadening of the propagative mode mainly comes from the broad $C_{22}(k,\omega)$ Ne-Ne correlations, whereas the peak in $C_{11}(k,\omega)$ can be followed up to the highest wave vector considered and its phase velocity can be scaled as $c_s(1) = c_s(M/M_1)^{1/2}$ in terms of the adiabatic sound velocity of the mixture and the mass ratio for the light component, which is in good agreement with that predicted for the fast kinetic mode

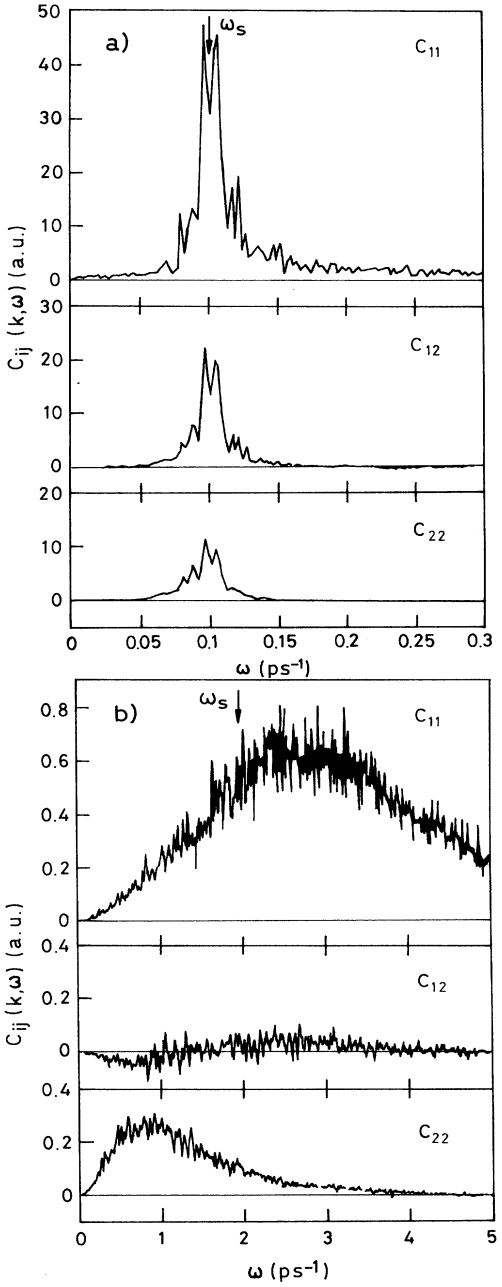

FIG. 3. $C_{ij}(k,\omega)$ for different wave vectors: (a) $k = 0.027$ Å^{-1} and (b) $k = 0.54$ Å^{-1}.

[3]. A similar scaling is possible for the heavy particle motions with $c_s(2)$ defined as $c_s(2) = c_s(M/M_2)^{1/2}$, and the overall behavior with k now agrees with that predicted for the slow kinetic mode of very dilute gases [4]. Also notice that the contribution of the heavy particles to the high frequency range of the spectra (i.e., the sound excitation) is reduced progressively with k. At large k values, $k > 0.2$ Å^{-1} the partial spectra are mostly decoupled, and the predicted total neutron scattering spectra agrees with that for the light component.

The wave-vector dependences of the Brillouin peak frequencies as well as that corresponding to maxima in the total $C(k,\omega)$ and partial $C_{ij}(k,w)$ spectra are shown in Fig. 4. If the maxima of the sound peak are plotted, departure from hydrodynamics sets in at $k = 0.06$ Å^{-1}, which shows a good agreement with the predicted value for k_h from the RET approach [9]. The presence of two kinetic modes can also be inferred if maxima of the longitudinal current spectra of both components are plotted. The latter functions become dominant within the microscopic regime (i.e., $k > 0.22$ Å^{-1}), in agreement with the theoretical value of 0.17 Å^{-1} obtained for dense He/Xe mixtures [3]. Notice, however, that such departure from hydrodynamics shifts to far higher k values if the maxima of the total current is considered instead, since the dressing of the bare frequencies by the damping terms preserves the linearity of the dispersion up to 0.22 Å^{-1}. In this case, the frequencies corresponding to the fast mode appear as some "positive dispersion" effect over normal sound. It becomes difficult to characterize in detail the kinetic modes because of the relatively large damping and the difficulties in a full separation between the components. From the shape of the dispersion curves shown in Fig. 4 it seems clear that the modes have a somewhat "optical" character and cannot be fully identified with sound propagation, even if the phase velocities of the excitations are close to those corresponding to a continuation to large wave vectors of hydrodynamic sound.

Finally, and as concluding remarks, the present communication has established the following.

(1) Dense gases formed by disparate mass particles show only one propagating collective mode at low wave vectors, the sound mode, accountable by linearized hydrodynamics.

(2) At intermediate wave vectors, the sound mode becomes considerably damped and its intensity decreases thus unveiling the presence of fast and slow modes, reflecting the uncoupled dynamics of both components. The relationship between the damping of the sound mode and the observation of kinetic modes are questions still open.

(3) The kinetic modes dominate the main features of the spectra at the microscopic scales. Within some restricted range of wave vectors, their phase velocities are close to that defined from the adiabatic sound velocity of the mixture modified by the mass of the pure components $c_s(i) = c_s(M/M_i)^{1/2}$.

(4) The RET approach for hard sphere, disparate-mass mixtures gives, at least qualitatively, an adequate description of the propagating modes present on actual mixtures. The main difference between its predictions and the present results regards the observed convergence of the two kinetic modes into the sonic one at low wave vectors, whereas the RET predicts the disappearance of the fast mode at these scales.

(5) Some manifestations of the kinetic modes seem amenable to NS experiments as excitations decoupled from the sound mode if the experimental window can reach the crossover wave vector k_h. By modifying the composition and the nature of the components, the total spectra should evidence the presence of the fast or slow kinetic modes.

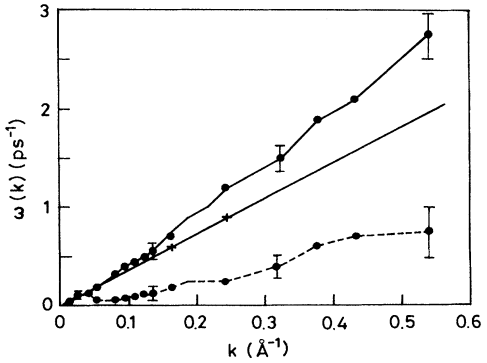

FIG. 4. Wave-vector dependence of the maxima of the propagating modes. Maxima of $C(k,\omega)$ [i.e., $\Omega_c(k)$, see text] (dots), fast kinetic mode obtained from $C_{11}(k,\omega)$ (solid line), slow kinetic mode obtained from $C_{22}(k,\omega)$ (dashed line). Sound peak frequencies of the partials observed as secondary peaks at intermediate wave vectors (crosses). The straight line shows hydrodynamic dispersion $c_s k$, with $c_s = 3.7$ Å ps^{-1}. Error bars estimated from the width of the peak plateaus.

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