Dynamic structure factor in a nonequilibrium fluid: A molecular-dynamics approach

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The dynamic structure factor for an Enskog gas subject to thermal constraints is studied both by molecular dynamics and by fluctuating hydrodynamics. Good quantitative agreement is demonstrated.

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Molecular dynamics (MD) has proved very useful for the study of statistical properties of fluids. For a long time this technique has been mostly devoted to equilibrium systems, using periodic boundary conditions [1]. Increasing computing capacity has permitted consideration of nonequilibrium systems as well [2]. One of the major achievements of nonequilibrium MD (NEMD) was the development of methods that allow the simulation of far-from-equilibrium states in periodic geometries, thus avoiding the perturbations due to the presence of boundaries [3,4]. There exists however a variety of problems that do not allow such treatments. This is specifically the case of microscopic simulation of systems exhibiting complex behaviors, as, for example, in the Rayleigh-Bénard problem [5], shock waves [6], or flows past an obstacle [7]. In all of these cases, one has to study fluids surrounded by thermal reservoirs or moving insulated walls. Given the fact that the scales reached in MD are extremely small, the question arises as to the influence of boundaries on the statistical properties of the system.

While it has been established that macroscopic hydrodynamics remains valid at these microscopic scales [8,9], not much is known about the behavior of fluctuations, especially in constrained geometries. The study of fluctuations is certainly the first step to understanding the microscopic mechanisms that are at the origin of macroscopic behavior of fluids, specially in the presence of instabilities. In any case, it is important to know whether the hydrodynamic model remains accurate to interpret the fluctuation spectrum. The present paper is devoted to this problem, both for equilibrium and nonequilibrium systems.

We consider an assembly of 1000 hard spheres that are allowed to move in a rectangular box of length L_x (in the x direction) and volume V. For practical convenience, lengths and masses are scaled by the sphere diameter d and the particle mass m, respectively, i.e., $d=m=1$. Similarly, by an appropriate scaling of time and velocities, the equilibrium temperature and the Boltzmann constant are set equal to unity. The box is confined between two rigid walls, located at $x=0$ and L_x, acting as infinite thermal reservoirs. Each time a particle hits a wall, it is reinjected into the system having its velocity sampled from a Maxwellian distribution at the wall temperature. Periodic boundary conditions are assumed in the other directions. The global number density will be set to 0.3 particles per d^3 and the aspect ratio L_x/L_y to 5, leading to a system length $L_x=43.68$ for $L_y=L_z$. We note that the hard spheres occupy 16% of the system volume; this corresponds to a moderately dense Enskog gas.

We start with an equilibrium system, i.e., we set equal temperatures in both reservoirs $T_0=T_L=1$. After the system has reached equilibrium, statistics are taken over 10^6 collision times (about 5×10^5 collisions per particle) in order to measure the Fourier transform of the Van Hove total correlation function, defined as

$$F_{\mathbf{q}}(t)=\langle n_{\mathbf{q}}(t)n_{-\mathbf{q}}(0)\rangle-|\langle n_{\mathbf{q}}\rangle|^2 , \tag{1}$$

where the brackets $\langle\ \rangle$ denote ensemble average and $n_{\mathbf{q}}$ is the Fourier transform of the number density:

$$n_{\mathbf{q}}(t)=\frac{1}{\sqrt{N}}\sum_{\alpha=1}^{N}\exp[i\mathbf{q}\cdot\mathbf{r}_\alpha(t)] . \tag{2}$$

Here N is the total number of particles and $\mathbf{r}_j(t)$ represents the position of the jth particle at time t. Note that the average density exhibits two peaks near the boundaries, the origin of which is a well-known consequence of particle–rigid-wall interactions [10].

To improve the statistics, q_y and q_z are set to zero, i.e., we limit ourselves to the study of "reduced" variables defined as the space average over y and z directions. Since the system is finite, the wave vector $\mathbf{q}$ can only take discrete values: $\mathbf{q}=q_x\mathbf{1}_X$, $q_x=2\pi k/L_x$, $k=1,2,\ldots$, where $\mathbf{1}_x$ represents the unit vector in the x direction. Given the small size of the system, we are forced to choose small values of k in order to remain in the hydrodynamic regime (typically $k=1$ or 2).

In Fig. 1 we represent the dynamic structure factor $S_q(\omega)$, also called *the scattering function,* defined as the time-Fourier transform of $F_q(t)$. The statistical error, estimated from successive runs of 10^4 collision times, does not exceed 8%. Besides the Rayleigh line, we observe two other peaks. The second one is the Brillouin line, centered roughly around $\omega=C_s 2\pi k/L_x$, where C_s is the sound speed (here $k=1$ and $C_s=2.44$ in system's units), whereas the first one, located at half the distance of the Brillouin line, reflects the finite-size effect. In macroscopic systems the presence of boundaries does not give rise to any measurable effect in the Rayleigh-Brillouin spectrum, at least in equilibrium [11]. This is not the case here, mainly because the distance between the containing walls remains smaller than the sound attenuation length (by about a factor of 4, for $k=1$). A sound wave, generated

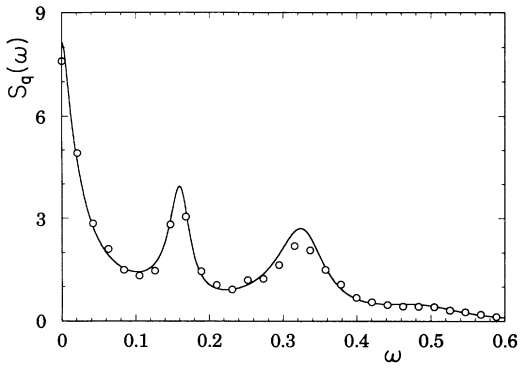

FIG. 1. Dynamic structure factor computed from MD (circles) and from fluctuating hydrodynamics in the equilibrium case ($T_0=T_L=1$).

through density fluctuations, will therefore be reflected several times by the boundaries before being damped through dissipative processes. As a consequence, one may expect standing sound waves across the system [12], which are at the origin of the extra peak observed in Fig. 1. Although the latter has been predicted theoretically for a liquid with a vanishing thermal expansivity coefficient [13], it is the first time that such a peak is seen through MD computations. To be sure of its origin, however, one needs to compare the measured spectrum with its theoretical counterpart, obtained through the numerical solution of the fluctuating hydrodynamic equations [14], using the method discussed in Ref. [15].

To proceed, we need the explicit form of the equation of state and of the transport coefficients of the fluid. For equation of state, we use the empirical Carnahan-Stirling relation, known to reproduce accurately the data computed in our range of densities [16]. For the transport coefficients, we use the expressions obtained from the first-order Chapman-Enskog solution of the Enskog equation [17]. The computed scattering function is also depicted in Fig. 1.

As can be seen, there is an excellent agreement between fluctuating-hydrodynamics and MD results. The agreement, however, becomes gradually less satisfactory as we consider higher values of the wave number, either by increasing k or decreasing the system length. The main reason for this discrepancy comes from the fact that we have used in our hydrodynamic equations an average uniform density profile, whereas a density boundary layer, extending roughly over one sphere diameter, has been observed in MD simulation. A full agreement with hydrodynamics can then only be expected for those fluctuations having wavelengths several times larger than the characteristic length of the boundary layer. This conclusion underlines also the fact that MD cannot be used for the study of small wavelength fluctuations, as described by generalized hydrodynamics [18], in systems which are in contact with rigid bodies.

Let us consider again the scattering function depicted in Fig. 1. A careful analysis of the data shows that the Brillouin peak is shifted to the left by about 8%, as compared to its theoretical value [11] $\omega=C_s 2\pi k/L_x$. The same remark holds for the finite-size peak which, according to the results of Ref. [13], must be located at half the distance of the Brillouin peak, i.e., at $\omega=C_s\pi k/L_x$. Although the physical origin of this shift is not clear at present, the numerical analysis of the fluctuating hydrodynamic equations for a wide range of parameters leads to the following conclusions: first, as the system size increases, the shift goes to zero, roughly as $L_x^{-1/2}$. Second, the origin of the shift seems to be crucially related on the coupling between the thermal modes and the sound modes. The subject clearly calls for more theoretical work.

Next, we consider nonequilibrium systems by setting unequal temperatures for the reservoirs. Several situations have been considered and for each case the computed temperature profiles are extrapolated to find the effective wall temperatures. The latter are found to be different from the corresponding imposed wall temperatures by about 4%. Note that this temperature slip is a well-known consequence of the thermalization procedure we have used in our MD simulation (stochastic thermal walls) [19,20]. The effective wall temperatures are then used as temperature-boundary conditions in the corresponding hydrodynamic equations which are solved numerically to give the macroscopic temperature and density profiles. Even for the strongest nonequilibrium situation we have considered (the temperature variation was about 4% over a sphere diameter), we find a perfect agreement with the measured profiles, except near the walls where a density boundary layer was observed, very much as in the equilibrium case.

Having established the validity of the macroscopic hydrodynamic equations, we next consider the fluctuations. Contrary to the equilibrium case, the imaginary part of the function $F_q(t)$ is found to be nonzero, indicating a broken time-reversal symmetry induced by nonequilibrium constraints. As a consequence, the structure factor exhibits an asymmetry with respect to ω. This is shown in Fig. 2, where $S_q(\omega)$ is depicted for $T_0=0.52$, $T_L=1.46$, and $k=1$ (the imposed wall temperatures were $T_0=0.5$ and $T_L=1.5$). The theoretical graph of $S_q(\omega)$, obtained from the numerical solution of the fluctuating hydrodynamic equations, is also depicted and, as can be seen, it shows excellent agreement with MD re-

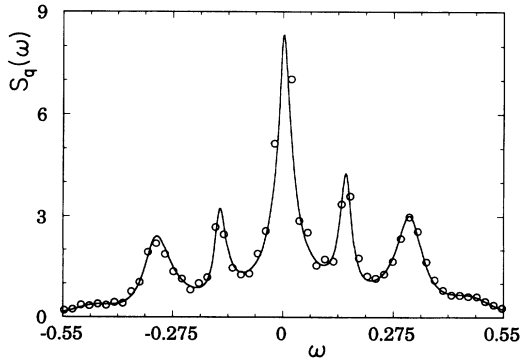

FIG. 2. Same as Fig. 1, for the nonequilibrium case ($T_0=0.52$, $T_L=1.46$).

sults. The same conclusion holds for all the values of temperature gradient examined, at least for $k=1$. Again, the agreement becomes gradually less good as we consider higher values of the wave number, precisely for the same reasons we have discussed in equilibrium case. Note that the finite-size peaks are also asymmetric, in qualitative agreement with the theoretical predictions of Ref. [13].

The asymmetry of the Brillouin lines was predicted by several authors a decade ago [21,22] and, later on, was confirmed through light-scattering experiments [23]. Unfortunately, the specific nature of the boundary conditions appropriate to our case, and the relatively small value of the wave number, does not allow a direct comparison with the existing theories. Nevertheless, some general conclusions can be drawn which may be used as a guideline for future theoretical works. First of all, the observed asymmetry is lower than the one predicted by neglecting the boundary conditions (infinite-system approximation), in qualitative agreement with the experimental [23] and theoretical results [12,24]. The precise determination of the discrepancy needs more numerical work and will be presented in the near future. Next, the asymmetry grows with the imposed temperature gradient. The rate of growth is linear for small values of the temperature gradient, but a deviation from linear regime is observed as the temperature gradient is increased [25]. Finally, we observe that the location of the Brillouin lines depends also on the temperature gradient, in qualitative agreement with the results of Refs. [21] and [25].

Let us now consider the Rayleigh line. Some time ago, extensive theoretical calculations, based on both mode-coupling theory [26] and fluctuating hydrodynamics [27], have shown that the amplitude of the Rayleigh line increases with the imposed temperature gradient $|\nabla T|^2/q^4$, provided the wave vector $\mathbf{q}$ is oriented perpendicular to the direction of the temperature gradient ∇T. More recently, the validity of the above prediction has been beautifully verified by Law and Sengers [28] through small-angle light-scattering experiments. From a theoretical point of view, it is generally believed that the main reason for the enhancement of the Rayleigh line is due to the coupling between transverse velocity fluctuations (parallel to the temperature gradient) and the entropy fluctuations. On the other hand, it is easy to show that the transverse fluctuations vanish in the limit $\omega \to 0$ (Rayleigh scattering), if the wave vector is parallel ∇T. For this reason, so far most of the existing theoretical and experimental work refers to the case of wave vectors perpendicular to the imposed temperature gradient, which is just the opposite of our choice of wave vector. Accordingly, we were expecting to find that in our computer experiments the Rayleigh line should remain quite insensitive to the imposed temperature gradient.

Surprisingly, the MD data show that, for a given wave number, the amplitude of the Rayleigh line grows quite accurately as the square of the temperature gradient, in perfect agreement with the numerical solution of the fluctuating hydrodynamics equations. On the other hand, the amplitude of the Rayleigh line decreases for increasing values of the wave number, roughly as $1/q^4$ for $k=1$, and switches to a $1/q^2$ dependence for higher values of k. This result confirms the existence of entropy (or temperature) long-range spatial correlations in nonequilibrium fluids, even though the coupling with the transverse velocity fluctuations is absent. Note that earlier particle simulations, based on a Monte Carlo simulation of the Boltzmann equation, have led precisely to the same conclusions, both for systems under temperature gradient and for systems under shear [29]. Similar results have also been obtained theoretically using a simple fluctuating Fourier type of equations [15,30]. To sum up, our work clearly indicates that the Rayleigh spectrum exhibits essentially the same type of behavior as the one observed experimentally by Law and Sengers for an opposite choice of the wave vector. It is therefore highly desirable to see whether or not an enhancement of the Rayleigh spectrum can be observed experimentally for a choice of the scattering vector parallel to the temperature gradient.

To conclude, we have reported here clear evidence of the validity of the fluctuating hydrodynamic formalism down to a few interatomic distances, even in the presence of extreme nonequilibrium conditions. Fluctuating hydrodynamics can thus be used with confidence for the study of fluctuations in nonequilibrium fluids, in the absence of instability. Our main goal in the future is to use NEMD to study the behavior of fluctuations in systems approaching convective instability, where the results of laboratory experiments are in total contradiction with those of the existing theories [31,32]. Whether or not fluctuating hydrodynamics remains accurate to describe the onset of such instabilities, is an open question (see, however, Ref. [33]). Works along this line are in progress.

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