Molecular dynamics of dense gases: Effects of continuous potentials

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Molecular-dynamics simulations of dense gases at 297 K (reduced temperature $T^*=T/\epsilon=1.47$) have been carried out using a Lennard-Jones (LJ) (6-12) pair potential and a truncated LJ potential. Our objective was to study the effects of continuous potentials, with and without attractive forces, on density fluctuations in dense fluids, and to interpret recent neutron scattering measurements on krypton gases which revealed significant deviations from results for hard-sphere fluids. We compare our results with experiments and other studies using molecular dynamics and kinetic theory, but which employed hard-sphere potentials. In particular, predictions of the full width at half maximum for $S(q,\omega)$ show improved agreement with experiments for values of $q<q_0$ where q_0 is the position of the first diffraction peak in $S(q)$, when the full potential is used. This satisfactory agreement verifies the sensitivity of the width of $S(q,\omega)$ to potential-dependent effects.

I. INTRODUCTION

It is a long held belief that the study of the dynamic structure factor $S(q,\omega)$ of a dense gas or a simple liquid will reveal aspects of thermal fluctuations which are sensitive to the details of intermolecular interactions.[1,2] From the standpoint of nonequilibrium statistical mechanics, the calculation of $S(q,\omega)$ is of considerable interest because it is one of the most fundamental observable quantities of a fluid system. From the standpoint of current studies in neutron and laser spectroscopy, the measurement of $S(q,\omega)$ provides an opportunity to test, at the molecular level, modern dynamical theories of simple fluids as well as to study transport phenomena at finite frequencies and wavelengths. For these reasons the problem of $S(q,\omega)$ has been the focal point of sustained theoretical and experimental efforts during the past two decades.[1-3] In a number of investigations computer molecular-dynamics simulation has played a unique role in elucidating the characteristic behavior of $S(q,\omega)$ of a liquid with Lennard-Jones interactions of hard-sphere fluids.[1,2,4]

Despite the fact that the general properties of $S(q,\omega)$ are well known, there exists no tractable theory for analyzing this function in fluids where the atoms interact via a continuous pair potential function having both a repulsive and an attractive part. For dilute gases $S(q,\omega)$ can be calculated by solving the linearized Boltzmann equation as an initial-value problem,[3] and results are known for hard-core interactions, Maxwell molecules (repulsive r^{-4} potential), and the Lennard-Jones potential. For dense fluids where imperfect gas behavior cannot be ignored a more general kinetic equation is needed.[3,5] In the case of hard spheres the Enskog equation, with a simple but essential modification, has been studied[6-8] and found to be valid up to quite high densities by comparison with simulation results.[4] On the other hand, a comparable theory for continuous potential functions is still lacking; consequently the effects of different potential functions on $S(q,\omega)$ have not been systematically analyzed.

An indication of potential related effects in $S(q,\omega)$ in dense gases was recently obtained from neutron scattering measurements on dense krypton gases at room temperature.[9] When the line-shape data were compared with calculations and simulation results for hard spheres, a significant difference in the wave-number variation of the linewidth of $S(q,\omega)$ was found. It seems reasonable to attribute this to differences in the dynamics of intermolecular collisions;[10] however, one cannot be certain of this interpretation without a full calculation using a realistic potential or a molecular-dynamics simulation.

The purpose of this paper is to present the results of a molecular-dynamics study of $S(q,\omega)$ in dense krypton gases at the same conditions as the neutron measurements. The simulation results obtained using a Lennard-Jones 6-12 potential are found to be in sufficient agreement with the neutron data to establish that the difference between neutron data and hard-sphere results indeed can be attributed to differences in the potential. Moreover, simulation results obtained using a truncated Lennard-Jones potential, a purely repulsive interaction, reveal that the attractive forces have an appreciable effect even at a temperature of 1.5 times the potential-well depth.

II. MOLECULAR-DYNAMICS SIMULATIONS

The simulations were carried out using standard molecular-dynamics techniques.[11] Newton's equations of motion for a system of N krypton atoms in a cubical box with periodic boundaries were integrated using a fifth-order predictor-corrector method. The potential function used was an effective two-body potential of the Lennard-Jones form, $V_{LJ}(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$, with $\sigma=3.57$ Å and $\epsilon=201.9$ K.[12] Additional runs were made using a

TABLE I. Molecular-dynamics simulations of krypton gas.

N	Potential	n^*	Steps
256	V_{LJ}	0.4872	4000
256	V_{LJ}	0.6279	4000
256	V_{LJT}	0.6279	4000
500	V_{LJ}	0.6279	4000
500	V_{LJT}	0.6279	4000

truncated Lennard-Jones potential, $V_{LJT}(r)=V_{LJ}(r)+\epsilon$ for $r \leq (2)^{1/6}$ and zero, otherwise. To keep the computations manageable the interatomic forces were cut off at $r=2.5\sigma$, which is typically between the second and third nearest neighbors in the fcc solid.

To begin a run, we first choose a density $n^*=n\sigma^3$, where n is the number density (atoms/m^3), and a reduced temperature $T^*=T/\epsilon$. Then we choose $N=4s^3$, $s=1,2,\ldots,$ which fixes the box size. The particles, arranged initially on a fcc lattice, are given velocities sampled from a random distribution and then continuously rescaled to the desired temperature until the system has reached equilibrium. Particle trajectories, $\vec{r}_i(t)$, $i=1,\ldots,N$, are saved and later analyzed to give the intermediate scattering function $F(q,t)$ and the static structure factor $S(q)$ as discussed below.

Results have been obtained at room temperature and two densities, $n=10.6\times10^{27}$ ($n^*=0.487$) and 13.8×10^{27} ($n^*=0.628$). Runs were made with $N=256$ and 500, to ascertain the effects of finite system size. Time step size was taken to be $\Delta t=0.005\tau$, where $\tau=\sigma(m/\epsilon)^{1/2}$ and $m=83.9$, the atomic mass. Parameters which describe specific simulations for which results will be given are summarized in Table I.

The time correlation function of interest is the intermediate scattering function

$$F(q,t)=\frac{1}{N}\sum_{i,j}\langle \exp[i\vec{q}\cdot\vec{r}_i(0)]\exp[-i\vec{q}\cdot\vec{r}_j(t)]\rangle ,$$

where $\vec{r}_i(t)$ is the position of particle i at time t, and $\langle\ \rangle$ denotes an ensemble average. The frequency transform of $F(q,t)$,

$$S(q,\omega)=\frac{1}{\pi}\int_0^\infty dt\cos(\omega t)F(q,t)$$

is the dynamic structure factor, the quantity that can be measured by neutron and light scattering. In practice we invoke the ergodic hypothesis and replace the ensemble average by an average over a number of time origins. The time origins were chosen sufficiently far apart to ensure a reasonable decay of statistical correlations. Typically time origins were separated by $10-20\Delta t$, and at least 150 origins were taken in computing values of $F(q,t)$. In addition, for a given value of q an average over a number of vectors $\vec{q}$ was made.

The static structure factor $S(q)$ is given by $F(q,t)$ at $t=0$. This quantity is quite sensitive to the amount of averaging taken; therefore, it is a good indicator of the reliability of the computed results.

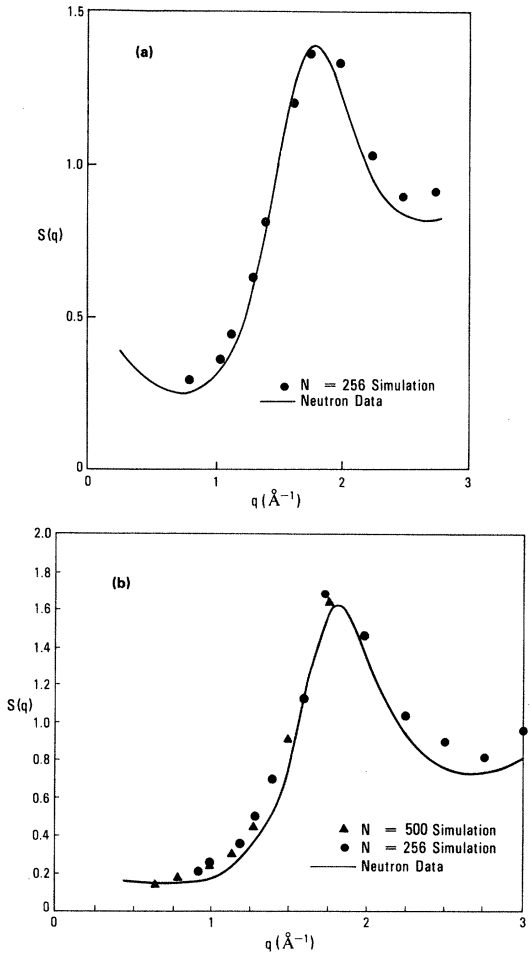

FIG. 1. Comparison of measured and calculated static structure factors $S(q)$ at (a) $n^*=0.482$ and (b) $n^*=0.628$.

III. RESULTS

The static structure factor $S(q)$ was obtained from the initial values of the intermediate scattering function. A comparison between our calculated values and the experimental data[9] is shown in Fig. 1 for the two densities. We have found that in computing $S(q)$ at different time origins, the results can fluctuate by as much as their own magnitude (which is usually of order unity); large fluctuations were more frequent at the lower gas density. We therefore relied on averaging over a large number of time origins to ensure reproducibility of the results. Generally, after about 150 time origins the cumulative average values of $S(q)$ fluctuated by less than 5% of their magnitude.

The effects of finite system volume, or equivalently the dependence on the number of particles are expected to show up in the small q regions of Fig. 1. When $2\pi/q$ becomes comparable to the box dimension, one can expect unphysical correlations caused by the periodic boundary conditions. Results for 256 and 500 particles are shown for the higher density system to indicate system size effects. Within the wave-number range that we can compare these results, no significant differences due to system size can be observed at the level of statistical averaging that was performed. Overall good agreement with the ex-

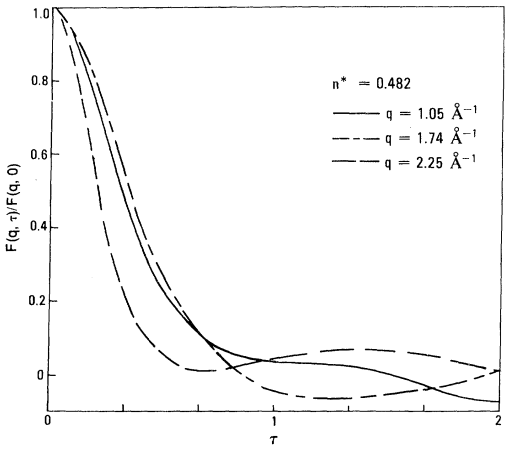

FIG. 2. Time dependence of the normalized intermediate scattering function $F(q,\tau)/F(q,0)$ at several wave numbers for $n^*=0.482$. ($q=1.05$, 1.74, 2.25 Å^{-1}.) Note use of $\tau=\sigma(m/\epsilon)^{1/2}$ as the time variable.

perimental data is seen, and at both densities the positions of the first diffraction peak are reasonably well predicted by the molecular-dynamics simulations.

The intermediate scattering functions for both gas densities are shown for several values of q in Figs. 2 and 3. For these comparisons the normalized values taken to be $F(q,\tau)/F(q,0)$ are used to observe better the time dependence. Note the use of τ as the time variable. In each case the initial rapid decay of $F(q,\tau)$ is followed by a much slower relaxation. For both densities there is a perceptible slowing down in the decay of $F(q,\tau)$ at wavelengths in the vicinity of the first diffraction maximum in $S(q)$. This is the de Gennes narrowing behavior which arises from strong spatial correlations.

The oscillations in the time correlation functions at larger times are believed to be unphysical. These fluctuations were examined in several instances by averaging over data generated from different initial velocity distributions. On this basis, the statistical fluctuations at long times

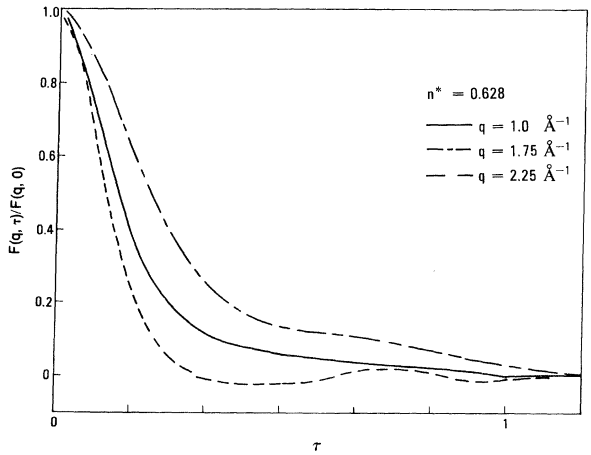

FIG. 3. Time dependence of the normalized intermediate scattering function $F(q,\tau)/F(q,0)$ at several wave numbers for $n^*=0.628$. ($q=1.00$, 1.75, 2.25 Å^{-1}.)

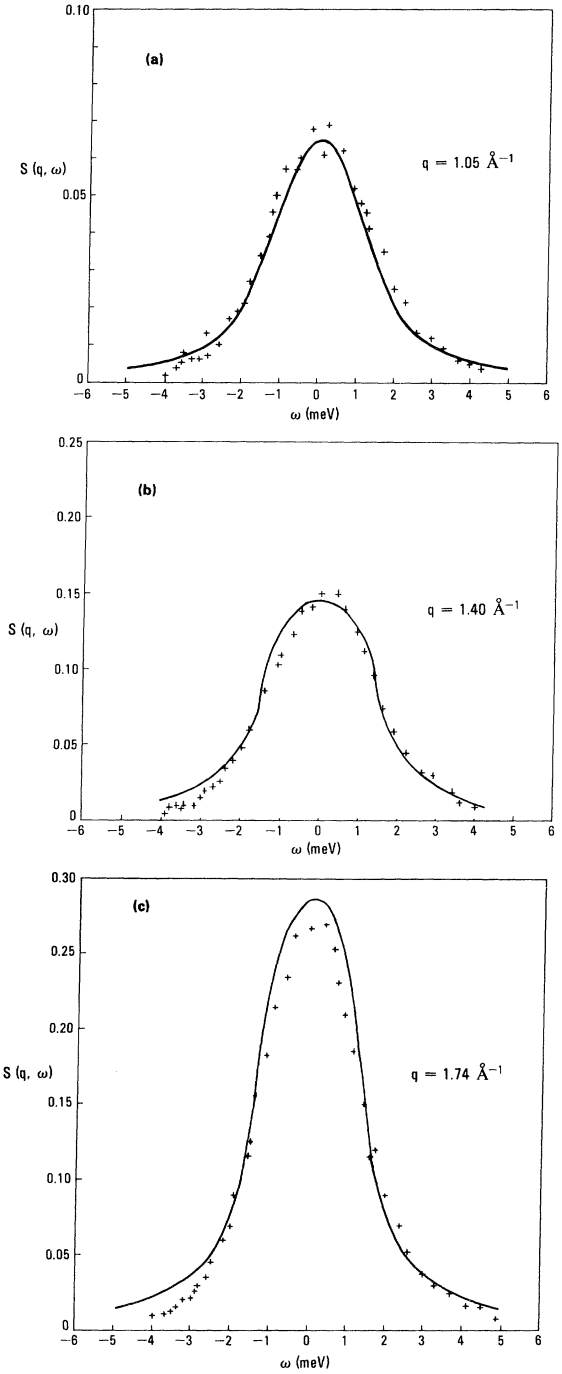

FIG. 4. (a) Comparison between calculated $S(q,\omega)$ ($N=256$) and measured spectra at $n^*=0.482$, $q=1.05$ Å^{-1}. (b) Comparison between calculated $S(q,\omega)$ ($N=256$) and measured spectra at $n^*=0.482$, $q=1.40$ Å^{-1}. (c) Comparison between calculated $S(q,\omega)$ ($N=256$) and measured spectra at $n^*=0.482$, $q=1.74$ Å^{-1}.

were found to be of the order of 0.04 or less.

Dynamic structure factors were obtained for a number of wavelengths at the two densities by Fourier transforming the time correlation functions. The time correlations were not smoothed before transforming; therefore, the resulting frequency spectra are influenced by statistical noise as well as by truncation of the data. The sensitivity

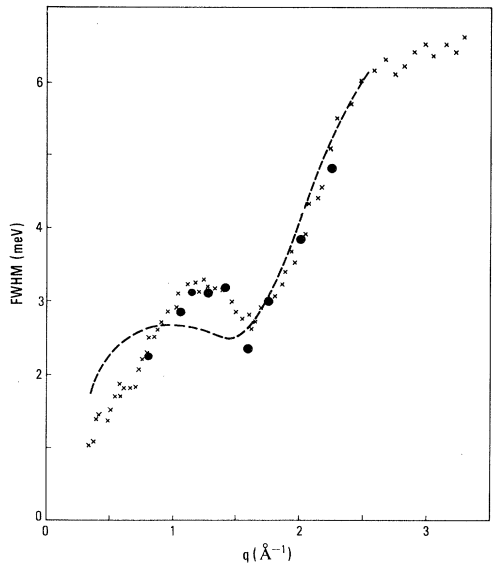

FIG. 5. Variation of $\Delta\omega$ with q at $n^*=0.482$. Crosses are neutron data corrected for resolution; dashed line is hard-sphere kinetic theory; and the circles are molecular-dynamics simulations using the V_{LJ} potential ($N=256$).

of our results to these effects was examined and will be discussed in turn below.

Comparisons between the calculated $S(q,\omega)$ and several measured spectra at $n^*=0.482$ are given in Figs. 4(a)—4(c). The frequency variable ω is expressed in meV. In general, the simulation results and neutron data are in good agreement. This is true even for the peak values $S(q,0)$ which can be sensitive to the truncation of $F(q,\tau)$, more so than the values of $S(q,\omega)$ at finite ω. Discrepancies between calculated and measured peak values were found to be of the same size as effects due to the finite truncation of the data.

Because the $S(q,\omega)$ spectra are all smooth functions, it is more revealing to characterize their behavior in terms of how the width varies with q. This also could be done with the peak heights, but as we have already noted, $S(q,0)$ exhibits a sensitivity to statistical noise and truncation of $F(q,\tau)$ which can make them less accurate than the full widths at half maximum. The uncertainty in the widths was estimated by examination of their sensitivity to the use of different time cutoffs in the correlation function data and in certain cases how reproducible they were from independent simulation data. Generally, the relative error in $\Delta\omega$ is less than $\pm$ 10%.

The variation of $\Delta\omega$ with q is shown in Fig. 5 for $n^*=0.482$. Experimental results, corrected for instrumental resolution, are given by the crosses, and the hard-sphere kinetic theory results of Dufty *et al.*[7] are shown as the dashed line. These kinetic theory results have been verified by hard-sphere molecular-dynamics simulations.

The general behavior of $\Delta\omega$ is what one can expect from previous studies,[2] $\Delta\omega$ increasing with q and a distinct dip occurring at the wave number where $S(q)$ has its first maximum. The dip is a characteristic structure in $\Delta\omega$ and signifies the intrinsic relation between $S(q,\omega)$ and $S(q)$; physically it means that the line shape of $S(q,\omega)$ is strongly influenced by the spatial correlations in the fluid. The appearance of this feature at the present density emphasizes that local spatial effects are important in the dynamics of gases at densities around the critical density.

As we can see in Fig. 5 the simulation results using the Lennard-Jones potential are in good agreement with the neutron data. For $1.5 \lesssim q \lesssim 2.5$ Å^{-1}, all the results agree including the hard-sphere kinetic theory calculations, thus suggesting that the dynamics of density fluctuations in this wave-number region is not sensitive to potential details. For $q \lesssim 1.5$ Å^{-1} the considerable difference between the Lennard-Jones potential and hard-sphere results confirms the sensitivity of $S(q,\omega)$ to potential details. Since the hard-core potential differs from V_{LJ} in several respects, we may ask what is the relative importance in the observed difference in $\Delta\omega$ between a repulsive potential with a finite range of interaction and the attractive part of the force derived from V_{LJ}. It is this question that motivated our repeating some of the simulations with a truncated Lennard-Jones potential V_{LJT}. This, however, was done only for the higher density system.

Figure 6 shows the results of simulations using the full and the truncated potentials at the density $n^*=0.628$. While the agreement between simulations using V_{LJ} and neutron data is generally improved over the hard-sphere results, some discrepancy still remains for $q<1.0$ Å^{-1}. We should emphasize that this discrepancy does not exist for the lower gas density results. In view of the V_{LJT} results, we can conclude that the use of continuous potentials produces two noticeable improvements in the differences between hard-sphere calculations and the neutron data. First, for wave numbers between 1.3 and 1.7 Å^{-1} the close agreement among the V_{LJ} and V_{LJT} simulations and the data suggests that the continuous nature of the repulsive potential plays an observable role in the dynamics. Second, below 1.2 Å^{-1} the V_{LJ} and V_{LJT} clearly separate with the V_{LJ} producing better agreement with the

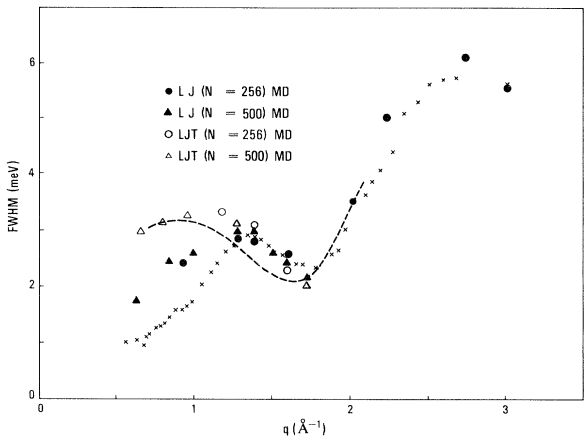

FIG. 6. Variation of $\Delta\omega$ with q at $n^*=0.628$. Crosses are neutron data corrected for resolution; dashed line is from hard-sphere kinetic theory; closed and open circles are molecular-dynamics simulations for 256 particles using the V_{LJ} and V_{LJT} potentials, respectively; closed and open triangles are molelcular-dynamics simulations for 500 particles using the V_{LJ} and V_{LJT} potentials, respectively.

neutron data. This strongly suggests that a significant part of the difference between hard spheres and V_{LJ} for $q < 1.2$ Å^{-1} should be attributed to the attractive forces. It is interesting that the V_{LJT} results turn out to be equivalent to hard-sphere calculations for $q < 1.2$ Å^{-1}, but are nearly commensurate with the V_{LJ} simulations above that wave number. One also should keep in mind that the magnitude of the effects discussed here is certain to vary appreciably with temperature.

The remaining discrepancy between V_{LJ} and the neutron data at low wave numbers (Fig. 6) does not have a clear explanation as yet. Additional study of the low-q dynamics using simulations at densities intermediate to those studied in this work might be worthwhile. In addition, the extension of a hydrodynamics description of $S(q,\omega)$ to sufficiently high wave numbers where a reasonable extrapolation to the low-q neutron data might be possible could be considered.

Finally, we note that for wave numbers around 3.0 Å^{-1} the molecular-dynamics results, although sparse, suggest the existence of a second dip in $\Delta\omega$, but additional calculations are needed to clarify the dynamics in this region.

IV. DISCUSSION

We believe the results presented in this work demonstrate that the line shape of $S(q,\omega)$ is sensitive to the details of intermolecular interactions in a dense gas. This conclusion is made possible by exploiting an essential advantage of molecular-dynamics simulation over laboratory experiments, that of isolating specific effects of potential functions by using different potentials in simulations which are identical otherwise.[13] Although the study of $S(q,\omega)$ in dense noble gases has been of interest for some time,[14–16] the particular linewidth sensitivity discussed here was first revealed in the recent neutron measurements on krypton.[9] The sensitivity in question appears in the regime of wavelengths short compared to values where hydrodynamic behavior of $S(q,\omega)$ dominates. (In the hydrodynamic regime one expects also significant difference between hard-sphere and Lennard-Jones fluids since the two systems have different equilibrium and transport properties.)

Further molecular-dynamics studies, especially at low-q values would be of interest, although computing costs would be higher because larger systems should be investigated. Also it would be useful to examine the effects of attractive forces at different temperatures; one expects generally an enhancement at lower temperatures.

The availability of molecular-dynamics data on $S(q,\omega)$ further emphasizes the need to develop a kinetic theory description of thermal fluctuations for dense fluids in which atoms interact via continuous potentials or potentials with attractive forces. Derivations of generalized kinetic equations for continuous potentials have been reported[17,18] but none of the analyses have been carried far enough to extract quantitative results for time correlation functions. The problem of deriving a tractable kinetic equation which treats properly the dynamics of two-body collisions in the presence of a continuous potential and the spatial correlations that exist in a dense fluid,[19] and the problem of analyzing such an equation, still remain a challenge.

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