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Short-wavelength collective excitations in liquids

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Abstract. During the last decade, important new information has been gained on the details of the dynamics in atomic liquids and gases on the molecular scale. This has primarily been the result of an intensive interplay between theory and improved inelastic neutron scattering (INS) experiments and computer molecular dynamics (CMD) simulations. A fruitful step in a better description of the dynamics of fluids has been the introduction of the concept of effective eigenmodes that can be determined from either hydrodynamic or kinetic theory or from a fit to observed (INS) dynamic structure factors or (CMD) time correlation functions. In this case a density fluctuation is built up from five separate contributions (lines) that take into account all possible correlations between five microscopic quantities (density n, velocity u, temperature T, longitudinal stress tensor σ, and heat flux vector q). The application of this model will be discussed for INS results on argon and CMD results of a Lennard-Jones fluid, recent INS experiments on fluid helium (at 13–39 K and 40–200 bar), where the dynamics are more complicated and strongly temperature dependent, and also recent neutron Brillouin scattering data on low-density ^{36}Ar gas.

1. Introduction

In this paper we are concerned with the understanding and description of the propagation and decay of local microscopic (wavenumber- and frequency-dependent) fluctuations in density, velocity, temperature, etc., in atomic liquids and dense gases and their computer counterparts. We consider, in particular, collective excitations with a short wavelength, i.e. $6\sigma \geqslant \lambda = 2\pi/k \geqslant 0.4\,\sigma$, or $1 \leqslant k\sigma \leqslant 15$, with σ the particle diameter. These can be studied experimentally with coherent inelastic neutron scattering (INS) and quasi-experimentally with computer molecular dynamics (CMD) simulations. With INS the dynamic structure factor $S(k, \omega)$ is obtained [1], which is the temporal Fourier transform of the density–density correlation (or intermediate scattering) function

$$F_{nn}(k,t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j(t)] \sum_{l=1}^{N} \exp[-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_l(0)] \right\rangle \tag{1}$$

with $\boldsymbol{r}_j(t)$ the position of particle j at time t. In CMD simulations, also other time correlation functions, unobservable in real experiments, can be obtained [2, 3]. This has been shown to be of great advantage in understanding the dynamics better.

The theories to describe the atomic dynamics as observed in INS or CMD have been developed either as a generalization of linear hydrodynamics or at the kinetic level [4, 5]. The kinetic theories are based on Enskog's modification of the Boltzmann equation for

hard spheres, which includes particle size effects and collisional transfer of momentum and energy. In particular, we want to refer here to the revised Enskog theory (RET) as developed and applied in the last 8 years [6] in an intensive interplay with both INS and CMD results of sufficient accuracy to make the confrontation with the theoretical model feasible [7]. The basic result of the theory is that the fluid behaves dynamically as if it possesses a few *effective eigenmodes*, the eigenvalues of which determine the decay rates of the thermal excitations, when they are real, and in addition their propagation frequencies, if they are complex. The eigenfunctions give the physical nature of the excitations.

In section 2 we summarize the results of an effective eigenmode analysis of INS results on dense fluid argon [8] and of CMD results on a dense Lennard-Jones (LJ) system [3]. Whereas $S(k, \omega)$ can be described as a sum of three Lorentzians, and equivalently $F_{nn}(k, t)$ as a sum of three exponentials (where the exponents are the eigenvalues and the intensities are determined by the eigenfunctions), other correlation functions turn out to be more sensitive to the details of the dynamics and need more modes for their description. For the studied argon and LJ states the coupling of density and velocity with the temperature fluctuations is important and $S(k, \omega)$ shows little structure, as opposed to liquid rubidium [9] where $S(k, \omega)$ shows clear side peaks and where a visco-elastic model is applicable [10]. In section 3 we refer to the question of how important the value of γ, the ratio of the specific heats, is for the observed differences, using recent INS data on supercritical helium [11]. In helium it is fairly easy to change γ from the Rb value of 1.1 to the Ar values of 2.0–2.9; for certain thermodynamic states, three modes are no longer sufficient to describe the dynamic behaviour, and even propagating short-wavelength temperature fluctuations are found. In section 4 we discuss the transition from the short-wavelength kinetic regime to the long-wavelength hydrodynamic regime using recent neutron Brillouin scattering data on ^{36}Ar gas [12].

2. Effective eigenmodes in argon and Lennard-Jones fluids

Effective eigenmodes render it possible to describe the short-wavelength dynamics of fluids over a large range of densities and wavevector transfers in a coherent way. These eigenmodes can be determined either from hydrodynamic or kinetic theory, or from a fit to observed (INS) dynamic structure factors or (CMD) time correlation functions. In the long-wavelength or small-k ($k\sigma \ll 1$) limit, observable with light scattering, $S(k, \omega)$ is obtained from the linearized hydrodynamic equations [4]. These describe the time evolution of fluctuations in the local number density n, the local longitudinal velocity u and the local temperature T (the slowest decay channels, connected with the conserved quantities). $S(k, \omega)$ is then given by a sum of three Lorentzians: the Rayleigh–Brillouin triplet with one central Rayleigh line due to the heat mode of the fluid and two side lines at $\pm \omega_s(k) = ck$ due to the two sound modes. Here c is the adiabatic sound velocity.

During the last 8 years it has been found that $S(k, \omega)$ for simple fluids as obtained for $k\sigma > 1$ from INS can also be described as a sum of three Lorentzians. This result was first derived from kinetic theory for hard-sphere fluids [6, 13] and was later confirmed by fits to INS data on argon [8, 14] and neon, and to CMD data on hard-sphere and LJ fluids [3, 6, 7]. For these states, $S(k, \omega)$ shows very little visible structure, except for small $k(<\sigma^{-1})$ or for Rb [9]. The physical nature of the Lorentzians (eigenmodes) for $k\sigma > 1$ has been investigated by kinetic theory [15], and also in much detail by the CMD of a LJ fluid at the triple-point density and reduced temperature $T^* = k_B T/\varepsilon_{LJ} = 1.7$,

with ε_{LJ} the LJ well depth [3]. Not only has $S_{nn}(k, \omega) = S(k, \omega)/S(k)$ been considered, but also other correlation functions $S_{jl}(k, \omega)$, or equivalently $F_{jl}(k, t)$, needed to understand $S(k, \omega)$ in detail.

It then appears that, in addition to the variables n, u and T, the fluctuations of the longitudinal stress tensor σ and of the longitudinal heat current q are needed. The set of all 25 correlation functions $S_{jl}(k, \omega)$ between j or $l = n, u, T, \sigma, q$ is given by [3, 11]

$$S_{jl}(k, \omega) = (1/\pi)\,\mathrm{Re}\{1/[\mathrm{i}\omega + \mathbf{H}(k)]\}_{j,l} \tag{2}$$

with $\mathbf{H}(k)$ the 5×5 symmetric matrix that describes the coupling between all five n, u, T, σ, q fluctuations. We refer to this as the thermal visco-elastic model [11], because it contains thermal relaxation (variables T and q) besides the pure visco-elastic model (with basic variables n, u and σ). The matrix $\mathbf{H}(k)$ has five eigenmodes which determine all 25 correlation functions $S_{jl}(k, \omega)$. Three of these modes are called the extended heat and sound modes, as they are the extensions of the hydrodynamic heat and sound modes (at $k\sigma < 1$, when the (n, u, T) fluctuations decouple from (σ, q)) to larger k-values. The two other modes of $\mathbf{H}(k)$ are of kinetic origin and have no hydrodynamic analogue. The dynamical processes in the fluid can thus be represented by five effective eigenmodes of the fluid as far as these 25 correlation functions are concerned.

Although all five eigenmodes are needed to describe all $S_{jl}(k, \omega)$ or $F_{jl}(k, t)$, it is found from the CMD simulations that $F_{nn}(k, t)$ can be represented by a sum of three exponentials, or equivalently $S_{nn}(k, \omega)$ by a sum of three Lorentzians, only. This is in full agreement with the earlier observations of satisfactory fits to INS and CMD data, mentioned earlier. The exponents of the exponentials determine the relaxation rates z_h and z_s of the extended heat and sound modes and the propagation frequency ω_s of the extended sound mode. For the nature of the modes, i.e. their amplitudes determined by the eigenfunctions, other correlation functions are needed as well. The values of z_h, z_s and ω_s as determined from fits to a sum of three or of five exponentials are virtually indistinguishable and are thus a good measure of the effective eigenmodes of fluids.

3. Collective excitations in supercritical helium

Whereas in an LJ fluid and in argon and neon the coupling of the density fluctuations with the temperature was found to be important, in liquid rubidium a visco-elastic model with the variables n, u, σ was applicable. In Delft, INS experiments have been performed on helium at six thermodynamic states with temperatures between 13 and 39 K, and pressures between 40 and 200 bar (n = 15–32 nm^{-3}; compare n = 18.7 nm^{-3} at 4.2 K and 1 bar) [11]. Then γ varies from 1.3 (close to the Rb value of 1.1) to 1.9, compared with the LJ value of 1.6 and the Ar values of 2.0–2.9.

It turned out that all six measured $S(k, \omega)$ can be described in a consistent way by equation (2), i.e. by the thermal visco-elastic model. At T = 39 K, n = 15 nm^{-3}, a pure visco-elastic behaviour was found, with irrelevant thermal relaxation and $S(k, \omega)$ given by three Lorentzians. At T = 24 K, n = 19 and 25 nm^{-3}, also three Lorentzians suffice; thermal relaxation is, however, relevant here and the nature of the lines is determined by all five basic variables. Very remarkably, at 13 K, n = 19, 25 and 32 nm^{-3}, all five Lorentzians of the model are needed to describe $S(k, \omega)$. A strong coupling was found of n and u with T, q and σ. The effective eigenmodes in these cases are an extended heat mode, two propagating extended sound modes and two propagating kinetic modes. For the sound modes the relaxation rate (damping) z_s is approximately equal to the

propagation frequency ω_s for $3\ \text{nm}^{-1} < k < 24\ \text{nm}^{-1}$, and the heavily damped side peaks are completely merged with the central peak. For the kinetic mode, z_k is slightly smaller than z_s, whereas $\omega_k \simeq 2\ \omega_s$, and clear side peaks are visible for $3\ \text{nm}^{-1} < k < 10\ \text{nm}^{-1}$. These side peaks turned out to be due to oscillating temperature fluctuations, visible in $S(k, \omega)$ because of coupling with density and velocity. As the eigenvalues and eigenfunctions were derived from the five-line fit to $S(k, \omega)$, $S_{TT}(k, \omega)$ could be calculated to support this analysis. It was found that both the extended heat mode (particle diffusion like beyond the hydrodynamic region) and the extended sound modes (mainly viscoelastic) have only weak components on T, and $S_{TT}(k, \omega)$ is mainly determined by clear peaks at ω_k due to propagating kinetic modes (T–q coupling).

4. Transition from the hydrodynamic to the kinetic regime in argon

In standard INS experiments the minimum k-values are about $2–3\ \text{nm}^{-1}$. These are outside the linear hydrodynamics regime as was observed in the noble gas and LJ fluids by the deviation of the k-dependence of the relaxation rates z_h and z_s from their hydrodynamic values of ak^2 and Γk^2, respectively, with a the thermal diffusivity and Γ the sound damping coefficient. To study the transition from the kinetic towards the hydrodynamic behaviour with decreasing k, recently neutron Brillouin scattering experiments were performed [12]. In order to reach sufficiently small k-values, in combination with good energy resolution, the IN5 spectrometer at Institut Laue–Langevin, Grenoble, was used with a two-dimensional position-sensitive detector covering scattering angles between 1.3° and 7.2°. The incident wavelength was 0.6 nm, the wavevector region $0.25\ \text{nm}^{-1} < k < 1.3\ \text{nm}^{-1}$, and the energy resolution 70 μeV. As a sample, ^{36}Ar gas was chosen. Because of the neutron scattering kinematics the sound velocity has to be at least 1.5 times smaller than the neutron velocity. This is the case for argon at room temperature and densities of 2.0 and $5.0\ \text{nm}^{-3}$ ($p = 80$ and 200 bar).

At the higher density, $S(k, \omega)$ changes gradually from a Rayleigh–Brillouin triplet at small k to a spectrum with broad side peaks. At the lower density the change is from a less well resolved triplet to a single central peak. All spectra could very well be fitted with a sum of three Lorentzians. The sound propagation frequency ω_s follows the hydrodynamic behaviour (ck) very well. The heat damping rate z_h, the sound damping rate z_s and the generalized specific heat ratio $\gamma(k)$ follow the hydrodynamic behaviour for the high density to at least $1.0\ \text{nm}^{-1}$, and for the low density to about $0.7\ \text{nm}^{-1}$. Thus a continuous transition from hydrodynamic into extended hydrodynamic (heat and sound) modes was verified.

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