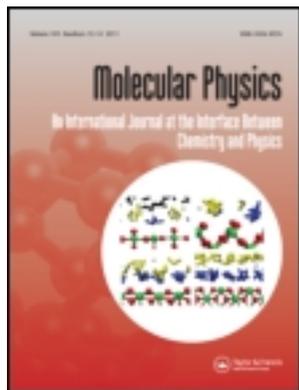


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Taras Bryk ^{a b} & Giancarlo Ruocco ^{c d}

^a Institute for Condensed Matter Physics, National Academy of Sciences of Ukraine, 1 Svientsitskii Street, 79011 Lviv, Ukraine

^b Institute of Applied Mathematics and Fundamental Sciences, National Technical University of Lviv, 79013 Lviv, Ukraine

^c Dipartimento di Fisica, Universita di Roma La Sapienza, I-00185, Roma, Italy

^d IPCF-CNR, Universita di Roma, I-00185, Roma, Italy

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INVITED ARTICLE

Generalized collective excitations in supercritical argon

Taras Bryk^{ab} and Giancarlo Ruocco^{cd*}

^aInstitute for Condensed Matter Physics, National Academy of Sciences of Ukraine, 1 Svientsitskii Street, 79011 Lviv, Ukraine; ^bInstitute of Applied Mathematics and Fundamental Sciences, National Technical University of Lviv, 79013 Lviv, Ukraine; ^cDipartimento di Fisica, Università di Roma La Sapienza, I-00185, Roma, Italy; ^dIPCF-CNR, Università di Roma, I-00185, Roma, Italy

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Dispersion and damping of collective excitations in supercritical argon along the isothermal line of 280 K are studied by a combination of molecular dynamics simulations and Generalized Collective Mode (GCM) analysis. ‘Positive dispersion’ of collective excitations and its dependence on density is discussed on the basis of GCM theory of ‘positive dispersion’.

Keywords: supercritical fluids; collective excitations; dispersion law; molecular dynamics; generalized collective modes; structural relaxation

1. Introduction

Collective dynamics in liquids and supercritical fluids is of renewed interest to the scientific community. Systematic improvements of the resolution in Inelastic X-ray Scattering (IXS) and Inelastic Neutron Scattering (INS) techniques [1,2] have made possible precise estimations of the dispersion of collective excitations in liquids as well as a search for the manifestation of non-hydrodynamic collective processes in dynamic structure factors $S(k, \omega)$, where k and ω are the wave number and the frequency, respectively. Very recently one of the most fascinating problems in collective dynamics of supercritical fluids has become the issue of the dependence of the so-called ‘positive dispersion’ of collective excitations on density. Outside the hydrodynamic regime the sound excitations in dense fluids have dispersion $\omega_s(k)$ which is no longer linear with wave number but bent up towards higher frequencies. This ‘positive dispersion’ of collective excitations was initially explained by mode coupling theory (MCT) [3,4]. The microscopic mechanism responsible for ‘positive dispersion’ in MCT [3] is the non-local (with different wave numbers) coupling of hydrodynamic relaxation and propagating modes. The MCT yields a correction to the hydrodynamic dispersion law of acoustic excitations $\alpha_s k^{5/2}$ with a positive prefactor α_s . This prefactor can be calculated from a sophisticated expression given in [5], that requires the knowledge of explicit density dependences

of adiabatic speed of sound $c_s(n)$ and thermal expansion coefficient $\alpha_T(n)$.

Recent IXS experiments performed on supercritical Ar at 573 K and subsequent MD simulations [6] showed that the positive dispersion in supercritical Ar decreased with the reduction of density and almost vanished at some density, which was associated with the Widom line extended into the supercritical region [7]. One of the consequences of this finding was a suggestion that the ‘positive dispersion’ can be a dynamic quantity that can discriminate between liquid-like and gas-like fluids in the supercritical region. However the calculations of density dependence of the MCT coefficient α_s for Ar at 573 K, which is responsible for the ‘positive dispersion’, were not in agreement with experimental findings, but supported previous calculations [5] for Ar at 120 K indicating an increase of α_s with decreasing density.

Recently a theory of ‘positive dispersion’ of collective excitations in fluids was developed within the method of Generalized Collective Modes (GCM) [8]. The essential difference between MCT and GCM is in the explicit treatment of the non-hydrodynamic processes in the GCM approach and their coupling with hydrodynamic modes in the local approximation [9,10]. Thus, due to coupling of collective excitations with a non-hydrodynamic process of structural relaxation, one obtains within the GCM analytical treatment the ‘positive dispersion’ of acoustic excitations on

*Corresponding author. Email: Giancarlo.Ruocco@roma1.infn.it

the boundary of the hydrodynamic regime [8]. Another interesting finding was the possibility of ‘negative dispersion’ of acoustic excitations due to their coupling with thermal processes. The GCM analysis of collective modes was performed in [8] for liquid Ar simulated with Lennard-Jones potentials at two temperatures 205 and 573 K. It was shown that the ‘positive dispersion’ vanishes with decreasing density for both temperatures, while ‘negative dispersion’ can appear for temperatures and densities by approaching the critical point.

An important issue is to study the ‘positive’ dispersion of collective excitations along more isothermal lines in the supercritical region. This would either support or discard the suggestion that the ‘positive dispersion’ vanishes by approaching the Widom line from the high-density side. Additionally, a problem in the simulations of the dynamic properties of supercritical fluids close to the critical point are finite-size effects. In [8] for the lower isothermal line corresponding to the temperature of 205 K a large deviation from the NIST data for the ratio of specific heats γ right at its maximum as a function of density was obtained, which could be a consequence of finite-size effects. Therefore in this study we aimed to check the relevant thermodynamic quantities obtained from the simulations with the NIST data in order to be sure that our simulations correctly reflected thermal processes in the supercritical fluid and then performed theoretical analysis of ‘positive dispersion’ based on the GCM approach. The remaining paper is organized as follows: in the next section we give details of the molecular dynamics simulations and consequent GCM analysis. The results on thermodynamic quantities and ‘positive dispersion’ for Ar at 280 K are reported in the third section, and the last section contains the conclusions of this study.

2. Molecular dynamics simulations

We performed MD simulations for 13 densities along the isothermal line $T=280$ K for supercritical argon using systems of 2000 particles interacting via *ab initio* Woon potentials [11]. Parameters of the potentials were taken from [12] and the cut-off radius was 12 Å. These potentials were the same as those used in MD simulations of supercritical Ar at 573 K [6]. The time step in the simulations was 2 fs. All the simulations were performed in the microcanonical ensemble. Energy conservation was at a very good level: the energy drift was less than 0.02% over the production runs of 480,000 time steps.

Every sixth configuration was used for sampling the dynamic variables. Dynamic variables of particle density, momentum density and energy density as well as their time derivatives needed for the GCM analysis were sampled for 30 different wave numbers directly in the MD simulations. The averages of the static and time correlation functions over all possible directions for different wave vectors with the same magnitude were performed.

The GCM analysis of the collective dynamics in supercritical argon was performed within a thermo-viscoelastic five-variable dynamic model:

$$\mathbf{A}^{(5)}(k, t) = \left\{ n(k, t), J^L(k, t), h(k, t), \dot{J}^L(k, t), \dot{h}(k, t) \right\}, \quad (1)$$

where $n(k, t)$, $J^L(k, t)$ and $h(k, t)$ are the Fourier components for the hydrodynamic variables of particle density, density of longitudinal component of current and heat density, and the overdots in the extended dynamic variables correspond to the first time derivatives of the hydrodynamic variables. Since the static average of the cross-correlations between a dynamic variable and its first time derivative is equal to zero, they are orthogonal, and the extension of the hydrodynamic basis set with the time derivatives of the hydrodynamic variables can be useful in describing non-hydrodynamic processes. Within the GCM approach the chosen extended set of N dynamic variables is used for the construction of the $N \times N$ generalized hydrodynamic matrix $\mathbf{T}(k)$, eigenvalues $z_i(k)$ of which correspond to wave-number dependent collective modes. Analytical solution of the thermo-viscoelastic dynamic model in the long-wavelength limit was obtained in [13].

The matrix elements of generalized hydrodynamic matrix $\mathbf{T}(k)$ can be expressed via wave-number dependent thermodynamic quantities, therefore for each density we estimated the following generalized thermodynamic quantities: generalized thermal expansion coefficient $\alpha_T(k)$, specific heat at constant volume $C_v(k)$, ratio of specific heats $\gamma(k)$, as well as regular static structure factor $S(k)$. We performed a check of the calculated thermodynamic quantities with the NIST database [14]. The long-wavelength limit of $C_v(k)$ was in perfect agreement with values C_v estimated from temperature fluctuations in the standard way. In Figure 1 one can see that the values of C_v calculated in MD are in good agreement with the NIST data. The values for the ratio of specific heats γ are within the acceptable 5% discrepancy with the NIST data, the calculated density dependence correctly reproduces the location of the maximum. Note that for C_p , the density dependence has its maximum at

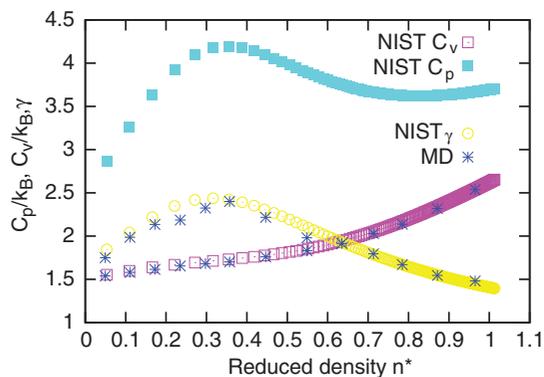


Figure 1. Specific heat at constant volume C_v and ratio of specific heats γ for Ar at 280 K calculated in this study (stars) in comparison with NIST data [14]. The dimensionless density was taken as $n^* = n * (3.405 \text{ \AA})^3$.

$n^* = 0.355$, i.e. for supercritical argon at 280 K the Widom line crosses the density dependences at $n^* = 0.355$. For convenience in comparison with Lennard-Jones systems the reduced density was taken as $n^* = n * (3.405 \text{ \AA})^3$.

The adiabatic speed of sound c_s was calculated from the long-wavelength limit of $[\gamma(k)/S(k)]^{1/2}$. In Figure 2 the calculated density dependence of the adiabatic speed of sound for supercritical Ar at 280 K is shown to be in good agreement with the NIST data. The adiabatic speed of sound increases monotonically with density having the most steep increase at high densities. An analytical expression for the density dependence of adiabatic speed of sound can be found in [15]. Another important quantity that usually is used in GCM analysis of collective dynamics is the high-frequency speed of sound c_∞ , which was estimated from the following expression

$$\lim_{k \rightarrow 0} \frac{\langle J^L(-k) J^L(k) \rangle}{\langle J^L(-k) J^L(k) \rangle} \propto c_\infty^2 k^2.$$

In Figure 2 it is shown that, in contrast to the adiabatic speed of sound, c_∞ increases almost linearly with density up to $n^* \sim 0.4$, while for high-density fluids it increases more steeply with density.

3. Results and discussion

We are mainly interested in dispersion of generalized sound excitations in supercritical Ar. Figures 3 and 4 show the dispersion and damping of collective excitations for two densities, obtained from the imaginary and real parts of complex eigenvalues in the GCM analysis of density–density, density–energy and energy–energy hydrodynamic time correlation

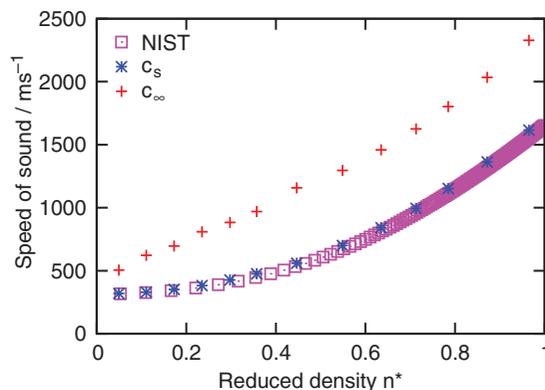


Figure 2. Calculated adiabatic (stars) and high-frequency (plus symbols) speeds of sound. The open boxes represent the adiabatic speed of sound for Ar at 280 K from the NIST database.

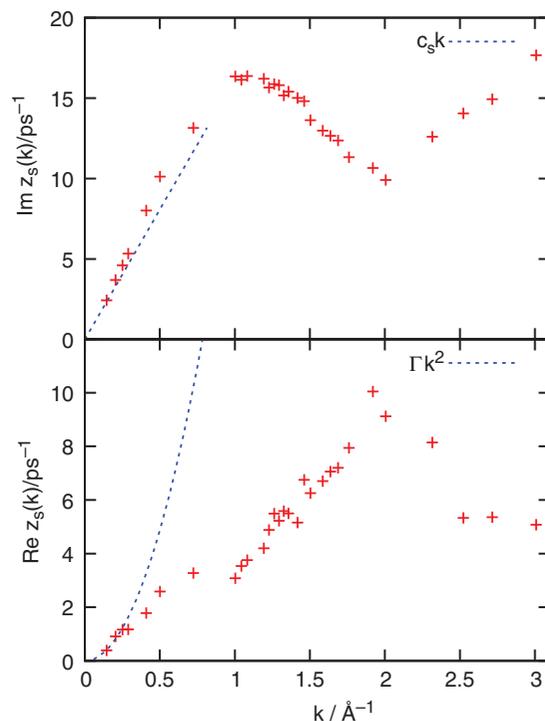


Figure 3. Dispersion and damping of generalized sound excitations for reduced density $n^* = 0.9648$. Dashed lines show the asymptotic hydrodynamic behaviour of dispersion and damping with calculated coefficients $c_s = 16.158 \text{ \AA ps}^{-1}$ and $\Gamma = 18.5 \text{ \AA}^2 \text{ ps}^{-1}$.

functions obtained from MD simulations. Matrix elements of the 5×5 generalized hydrodynamic matrix $\mathbf{T}(k)$, constructed on the basis set of dynamic variables (1), were calculated via static and time correlation functions for each wave number. No fit

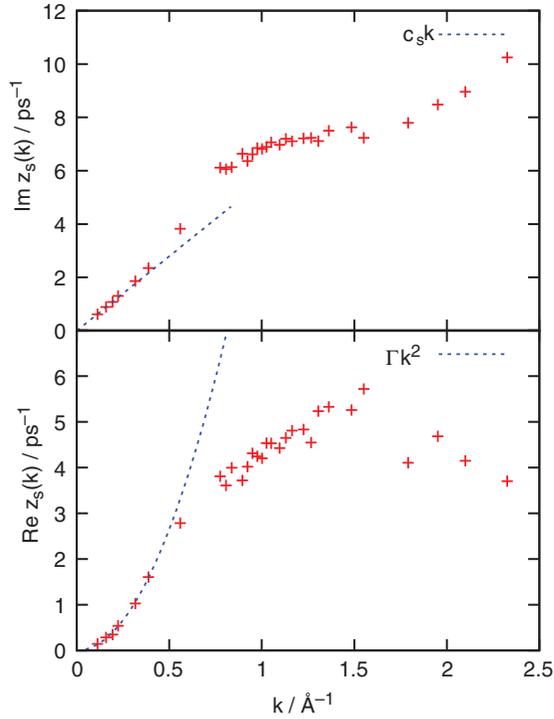


Figure 4. Dispersion and damping of generalized sound excitations for reduced density $n^* = 0.4465$. Dashed lines show the asymptotic hydrodynamic behaviour of dispersion and damping with calculated coefficients $c_s = 5.584 \text{ \AA ps}^{-1}$ and $\Gamma = 10.6 \text{ \AA}^2 \text{ ps}^{-1}$.

parameters were used. The solution of the eigenvalue problem for $\mathbf{T}(k)$ corresponds to dynamic eigenmodes that can exist in some frequency windows and a given wave number k in the studied fluid. In the long-wavelength region the standard three hydrodynamic modes were recovered: the real eigenvalue with long-wavelength asymptote

$$d_1(k) = D_T k^2, \quad (2)$$

where D_T is thermal diffusivity, and a complex-conjugated pair of eigenvalues corresponding to hydrodynamic sound:

$$z_s(k) = \Gamma k^2 \pm i c_s k, \quad (3)$$

where $\Gamma = (D_L + (\gamma - 1)D_T)/2$ is the sound damping coefficient, and D_L is the kinematic viscosity. The hydrodynamic long-wavelength asymptotes for sound excitations (3) are recovered for GCM eigenvalues as shown in Figures 3 and 4. One can see that the region of wave numbers, where the GCM sound eigenvalues reach the hydrodynamic asymptotes, depends on density: for high-density fluids it is quite narrow and it increases with reduction of density. This is evidence

of different strengths of processes responsible for the emergence of ‘positive dispersion’ of collective excitations.

One has to note, that in the long-wavelength region the imaginary parts of complex eigenvalues $\text{Im } z_s(k)$ exactly correspond to the frequency of the side peak of dynamic structure factor $S(k, \omega)$. However beyond the hydrodynamic regime the side peak position is not exactly equal to $\text{Im } z_s(k)$ because of other contributions to $S(k, \omega)$ like the asymmetric (non-Lorentzian) one, which increases linearly with k in the long-wavelength region and becomes quite important beyond the hydrodynamic regime [16]. Additionally, non-hydrodynamic excitations like heat waves or ‘fast sound’ in binary melts with disparate masses make non-zero contributions to the dynamic structure factors measured in scattering experiments. Experimental estimation of sound dispersion via Brillouin peak position of $S(k, \omega)$ is based solely on the hydrodynamic picture of collective dynamics, while more sophisticated models are needed for the analysis of experimental $S(k, \omega)$ with the purpose of estimating the true sound dispersion.

Among the five eigenmodes, obtained in the long-wavelength region two real eigenvalues tend to non-zero values in the $k \rightarrow 0$ limit, which is evidence that they belong to non-hydrodynamic processes with finite lifetime on macroscopic distances, i.e. they do not survive on the macroscopic scale in comparison with hydrodynamic processes. The analytical solution for the five-variable dynamic model was obtained in the long-wavelength limit in [13], and expressions for the two long-wavelength non-hydrodynamic (kinetic) modes read:

$$d_2(k) = d_2^0 - D_L k^2 + (\gamma - 1) \Delta k^2, \quad (4)$$

and

$$d_3(k) = d_3^0 - \gamma D_T k^2 - (\gamma - 1) \Delta k^2, \quad (5)$$

where the $k=0$ values are:

$$d_2^0 = \frac{c_\infty^2 - c_s^2}{D_L}$$

and

$$d_3^0 = \frac{c_V}{m\lambda} \left[G^h - \frac{(\gamma - 1)}{\kappa_T} \right].$$

Here

$$\Delta = \frac{d_2^0 d_3^0}{d_3^0 - d_2^0} \frac{D_T}{D_L c_s^2} (D_T - D_L)^2$$

is a coefficient that reflects coupling between the two non-hydrodynamic modes. The quantities G^h and κ_T

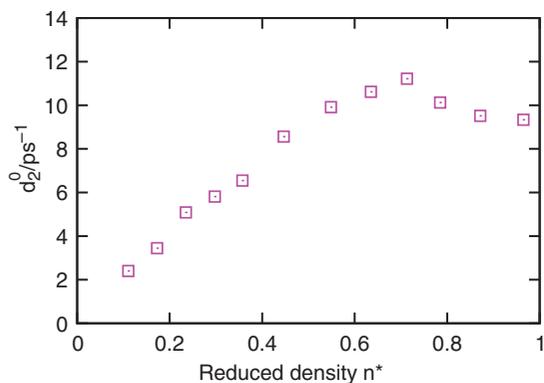


Figure 5. Dependence of the long-wavelength limit of the structural relaxation mode on density for supercritical Ar at 280 K.

correspond to heat rigidity modulus and isothermal compressibility, respectively. Because of the factor $(\gamma - 1)$ the last terms on the right-hand sides of (4) and (5) appear only due to coupling between the heat and density fluctuations. The quantity $(c_\infty^2 - c_s^2)$ is referred to in the literature as the strength of structural relaxation and for wave numbers in the vicinity of the first sharp diffraction peak it is possible to show that $d_2(k)$ is the inverse relaxation time of the cage of nearest neighbours [17]. Namely the non-hydrodynamic mode $d_2(k)$ reflects the structural relaxation in fluids. The other non-hydrodynamic mode, $d_3(k)$, is of thermal origin, it keeps information about heat rigidity in the fluid, and as shown in [18] the non-hydrodynamic process $d_3(k)$ for increasing wave numbers is responsible for the emergence of non-hydrodynamic heat waves which can exist on nano-scales but not for macroscopic distances and times.

The ‘positive dispersion’ of collective excitations appears mainly due to interaction of acoustic modes with structural relaxation on the boundary of the hydrodynamic regime. In Figure 5 we show how the strength of structural relaxation changes with density. In the high-density region there is a maximum that appears because of a faster drop in kinematic viscosity D_L with reduction of density than with the change in $(c_\infty^2 - c_s^2)$. Further decrease of density leads to monotonic decay of d_2^0 which implies that even for low density fluids the non-hydrodynamic mode $d_2(k)$ will have quite a large relaxation time and therefore will be important in the collective dynamics of low-density fluids too. On the other hand the elastic properties of the system monotonically decay with decreasing density, as seen from Figure 6, where the high-frequency shear module G_∞ and bulk module K_∞ are shown.

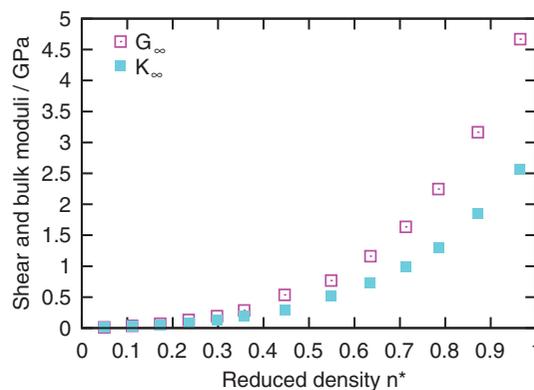


Figure 6. Dependence of the high-frequency shear and the bulk moduli on density for supercritical Ar at 280 K.

Within the GCM theory the ‘positive dispersion’ can be obtained as a long-wavelength correction to the hydrodynamic dispersion law which is proportional to k^3 [8]

$$\omega_s(k) \approx c_s k + \beta k^3 + \dots \quad (6)$$

with the prefactor β that reads:

$$\beta = \frac{c_s D_L^2}{8} \frac{5 - (c_\infty/c_s)^2}{c_\infty^2 - c_s^2} - (\gamma - 1) D_T \left[\frac{6D_L + (\gamma - 5)D_T}{8c_s} - \frac{c_s}{2a_3^0} \right]. \quad (7)$$

For the viscoelastic approximation, when the ratio of specific heats $\gamma = 1$, one obtains a very simple expression for the dispersion of the collective excitations on the boundary of the hydrodynamic regime:

$$\omega(k) \approx c_s k + \frac{c_s D_L^2}{8} \frac{5 - (c_\infty/c_s)^2}{c_\infty^2 - c_s^2} k^3. \quad (8)$$

It follows from this expression that, depending on the ratio of high-frequency speed of sound to adiabatic speed of sound, one can obtain even vanishing to zero ‘positive dispersion’ and possible ‘negative dispersion’. From Figure 2 one can see that the largest ratio of the high-frequency speed of sound to the adiabatic one, c_∞/c_s , is larger than 2 and takes place between densities $n^* = 0.4465$ and $n^* = 0.2351$, which implies almost vanishing ‘positive dispersion’ in that region of densities. In Figure 7 one can see how the positive dispersion reduces with decreasing density. According to the NIST database for argon [14] the Widom line crosses the isotherm $T = 280$ K at $n^* = 0.357$ which is in agreement with Figure 7, where the ‘positive dispersion’ almost vanishes on approaching that density. Another interesting finding is a small increase of

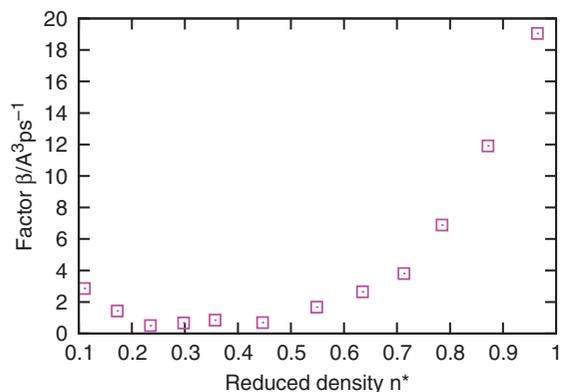


Figure 7. Density dependence of the factor β (6) for ‘positive dispersion’ of collective excitations in supercritical Ar at 280 K as calculated within the viscoelastic approximation.

the ‘positive dispersion’ for very low-density fluids, which within the adopted approximation in our GCM analysis is explained by decreasing for very low density systems the ratio between the high-frequency sound and the adiabatic one. Note that the analysis of IXS experiments on Ar at 573 K in [6] gave evidence of a small ($\sim 4\%$) ‘positive dispersion’ even in the low-density region.

4. Conclusions

We performed a combined study based on MD simulations of supercritical Ar along the isothermal line of 280 K and theoretical GCM analysis of collective excitations. We made check that our calculated density dependences of adiabatic speed of sound, ratio of specific heats and specific heat at constant volume were in good agreement with the NIST data. Based on these quantities we studied the ‘positive dispersion’ of collective excitations in supercritical Ar and how it depends on density.

We made use of the five-variable dynamic model for GCM analysis of time correlation functions obtained in MD simulations. We found, that the ‘positive dispersion’ reduces with decreasing density. The theoretical GCM expression for the correction to the hydrodynamic dispersion law yields ‘positive dispersion’ in good agreement with the MD data over a wide region of densities. We found, that the theoretical expression for ‘positive dispersion’ is in agreement with

a suggestion that the ‘positive dispersion’ can vanish in the vicinity of the Widom line [6].

Acknowledgements

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