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Collective particle motions in molten KCl

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Abstract

By means of inelastic X-ray scattering we measured the acoustic-type particle fluctuations in the molten alkali halide potassium chloride. From inelastic excitations in the spectra we derived a dispersion relation, which shows a large positive dispersion effect with a phase velocity exceeding the adiabatic value by about 50%. This frequency enhancement could be related to a more solid-like behaviour at high frequencies. Surprisingly, the derived dispersion resembles the acoustic modes of the liquid metal potassium.

Keywords: Molten salts; X-ray scattering; Collective dynamics

1. Introduction

Molten salts are applied in many technologically relevant areas. Traditionally they appear in electrochemical processes as, e.g. in high temperature fuel cells. Nowadays further applications are emerging due to their interesting thermophysical properties, e.g. large range of the liquid state, high specific heat, low vapor pressure and high critical points. One application may be the use of molten salts as fuel and coolant in a next generation nuclear reactor, the molten salt reactor, or the subsequent fission product recycling [1]. Another use is the heating of molten salts in solar power plants [2]. Mirrors collect the solar energy to a receiver tower where the molten salt stores the energy. The heat can then be transferred to a water circuit for conventional power production. The use of molten salt as storage medium guarantees the availability of electrical power further on into times without sunshine. All these applications require as input thermodynamic parameters, like specific heat and thermal conductivity. The excitations and hence the density of states are the input quantities for the specific heat. The lifetime of the excitations is related to thermal conductivity and viscosity. We are here concerned with the microscopic origins of these thermodynamic quantities.

The study of binary ionic liquids and as prototypes of them, the molten alkali halides, has a long tradition in theory and simulation [3]. Molecular dynamics (MD) groups have early investigated ionic liquids due to their simple attractive potential. From structural point of view coulomb liquids exhibit short range order due to the electrical charge, which shows an alternation in charge of the successive coordination shells around a central ion. Neutron scattering experiments, applying isotopic substitution, measured the partial structure factors [4] and the derived pair distribution functions show maxima at changing distances up to a radius of about 12 Å [5]. This solid-like structural arrangement is probably responsible for the peculiar dynamic response, which resembles the solid state, too. One prominent feature in the dynamics is the prediction of optic modes as was shown in the pioneering computer simulation of a simple molten salt by Hansen and McDonald more than 30 years ago [6]. On the other side their data gave no hints for propagating acoustic modes, a result which was attained several times later on in MD-simulations [7,8]. With inclusion of ion polarization, as was shown for NaI, indications for propagating density fluctuations were found as shoulders at the smallest attainable Q-vectors [9]. The fact that polarization might play a fundamental role in alkali halide dynamics was already recognized after the first phonon measurements with neutrons on alkali halide crystals [10]. The failure of the data description with lattice dynamical models using rigid-ion potentials has led to the introduction of the shell model [11]. In this model an electron cloud is harmonically

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bound to the core and can be shifted against the core position. The inclusion of ion polarization improved the lattice dynamical calculations distinctly.

During the last decades investigations on collective dynamics of liquids focussed mostly on elements, as, e.g. liquid metals (for a recent review see, e.g. [12]). The detected excitations can be understood as high frequency propagating sound modes, due to their linear dispersion at small Q-vectors. The collective dynamics of two component liquids was rarely experimentally studied until now. One reason for this might be the wealth of information one gets in a single scattering experiment, which is often difficult or even impossible to separate into the individual interesting components. The measured intensity of a two component liquid can be expressed as a combination of three scattering functions. An appropriate choice for the scattering functions in ionic liquids is based on density and charge fluctuations. In this notation the measured intensity $I(Q,\omega)$ is given in the following form [13]:

$$I(Q,\omega) \propto (f_+ + f_-)^2 S_{NN}(Q,\omega) + (f_+^2 - f_-^2) S_{NQ}(Q,\omega) + (f_+ - f_-)^2 S_{QQ}(Q,\omega) \tag{1}$$

$S_{NN}(Q,\omega)$ describes the particle density fluctuations and $S_{QQ}(Q,\omega)$ is determined by charge fluctuations. The cross term $S_{NQ}(Q,\omega)$ is for small Q-vectors a small quantity and can often be neglected compared to the other two functions. The scattering function $S_{NN}(Q,\omega)$ denotes the contribution for movements of the ions in phase and is therefore related to acoustic modes. $S_{QQ}(Q,\omega)$ contributes to the measured intensity, if the different charged ions move out of phase and the excitations are called optic modes.

The prefactors in Eq. (1) are sums or differences of atomic form factors or in the neutron case the coherent scattering lengths. All three scattering functions normally contribute to the measured signal. In neutron scattering one can choose different isotopes in certain cases and change the prefactors to select a particular scattering function. This method has been applied to get partial structure factors and later also in the inelastic case to search for optic or acoustic modes in molten salts [4,5]. For inelastic X-ray scattering this possibility does not exist in general, however, for alkali halides one can choose compositions like potassium chloride or sodium fluoride – neighboring elements – which have the same number of electrons per ion. Then the second and third term in Eq. (1) cancel out and one measures the particle density fluctuations without disturbance of the other contributions over the whole momentum transfer range. Due to the different size of the ions the atomic form factors decrease in a different way. For KCl the difference between the K^+ and the Cl^- form factors is less than 1.5 electron charges for higher Q-vectors [14]. For inelastic measurements this difference can surely be neglected, because only the squared form factors contribute to the intensity.

Neutron scattering groups have intensively investigated the ion dynamics in molten salts and searched for the expected optic modes (for a review see, e.g. [5]). However, inelastic neutron scattering experiments are always restricted in the kinematic accessible range. Therefore, most of the available experimental data were obtained at momentum transfers beyond $10\,\mathrm{nm}^{-1}$ [5,15]. No evidence of propagating acoustic-like modes could be observed in the spectra directly, because at these relatively large Q-values the lifetime of an acoustic mode might be already too short. However, at quite small momentum transfers Brillouin light scattering showed propagating acoustic modes in the GHz regime with a sound velocity of 1600 m/s in molten KCl [16]. This velocity is nearly unchanged compared to the results of ultra sound methods [17]. Recently, we measured molten NaCl with inelastic X-ray scattering and observed acoustic-like excitations directly in the spectra [18]. Inelastic X-ray scattering has no kinematic restrictions, hence it allows to measure large energy transfers of the scattered photons even at small Q-values. Surprisingly, the derived dispersion of molten NaCl resembled the dispersion of liquid sodium. The puzzling question emerged whether there is a decoupling of ion dynamics at high frequency. According to Eq. (1) in NaCl not only the acoustic-like fluctuations contribute to the signal but also the charge fluctuations, which complicates the assignment of the different modes. Therefore, we chose a compound, where mostly the acoustic-like term appears in the scattered intensity, namely KCl.

2. Experiment

The experiment was carried out at the inelastic beamline ID28 of the European Synchrotron Radiation Facility, ESRF, in Grenoble. X-rays were highly monochromatized to 21.747 keV using the Si (11 11 11) reflection in near back scattering. The incoming energy is changed by a thermal change of the lattice parameter, which has to be achieved within a mK stability range. Five silicon crystal assembles, using the same back scattering conditions, analyzed the scattered radiation. The energy resolution of the spectrometer was determined from the scattering of a Plexiglas sample to about 1.7 meV (full width at half height). The sample was contained in a single crystal sapphire cell with a wall thickness of 0.25 mm and a sample thickness of 0.5 mm was chosen. The sample environment consisted of an internally heated vessel equipped with Be windows. High temperatures were generated with a molybdenum resistance heater mounted around the sample volume [19]. The construction has the inherent advantage that the salt is stored in a reservoir and can be kept solid during the high temperature empty cell measurements. Upon melting the salt will be pressed into the sample area with helium gas. No new installation and possible change in the position of the cell is necessary. A constant helium pressure of about 1–2 bar inside the autoclave is necessary during the measurements against the vapor pressure of the molten salt. Empty cell measurements were carried out separately using the same cell at the same temperature $T = 1070\,\mathrm{K}$. For nine different Q-values between 2.6 and $14.4\,\mathrm{nm}^{-1}$ $S(Q,\omega)$ spectra were measured at 1070 K (melting temperature of KCl: $T_{\mathrm{melt}} = 1049\,\mathrm{K}$). In the interesting low momentum transfer region, up to five scans with about 1 min per scan point have been performed. The typical energy step size was about 0.25 meV and the covered energy transfers ranged from −40 to +40 meV. In Fig. 1 four spectra are shown. In the plot with $Q = 4\,\mathrm{nm}^{-1}$ the resolution function is included as a dashed line. The acoustic-like collective excitations are visible as shoulders in the spectra. In the picture for the smallest Q-vector the sapphire phonons from the container contribution appear at large energy transfer. However, due to the high sound velocity in sapphire ($c \approx 11,000\,\mathrm{m/s}$) these modes lie far outside the analyzed energy range and do not influence the reported results. The data have been symmetrized by multiplication with $\exp(-\hbar\omega/2k_{\mathrm{B}}T)$. To extract the properties of the collective excitations from the measured intensity the data were fitted to a model function. To describe the line shape of the liquid we apply the so called viscoelastic model, which was already used in the early MD-simulations to describe the line shape [6]. The model can be derived from a generalized Langevin equation, where a constant friction coefficient is replaced by a time dependent memory function. With the assumption of an exponential decay of the memory function one eventually gets the following functional

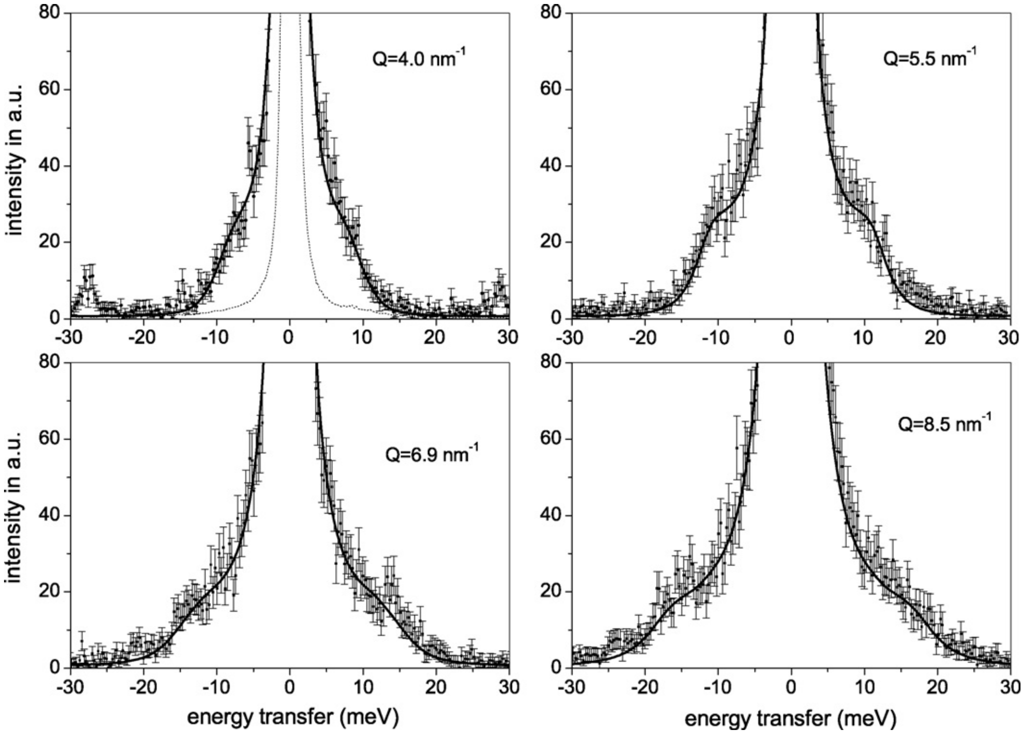

Fig. 1. $S(Q, \omega)$ spectra of molten KCl are shown in a linear scale. The thick line is the fit of the model function to the data. In the spectrum of $Q = 4\,\text{nm}^{-1}$ the measured resolution function is included as a dashed line. In addition, the fit model functions convoluted with the spectrometer resolution are plotted.

form [20]:

$$S(Q,\omega)=\frac{S(Q)}{\pi}\frac{(\omega_l^2-\omega_0^2)\tau(Q)\omega_0^2}{\omega^2\tau^2(Q)(\omega^2-\omega_l^2)^2+(\omega^2-\omega_0^2)^2} \qquad (2)$$

Besides the structure factor $S(Q)$ and the relaxation time $\tau(Q)$ there appear two further parameters: $\omega_0^2(Q)$ and $\omega_l^2(Q)$, which are both related to the frequency moments of the dynamic structure factor. From this equation one can deduce: if high frequencies are probed compared to the inverse relaxation time then the poles of the denominator are given by ω_l^2, which then defines the dispersion relation. The fitting procedure included a convolution with the spectrometer resolution function which was represented by a PseudoVoigt-function. A constant background of 0.8 in the scale of Fig. 1, deduced from the empty cell measurements, has been included into the fit procedure. The fit range was restricted to energy values without disturbance by the acoustic sapphire phonons.

3. Results and discussion

Results of the fits are shown in Fig. 2 for the frequencies $\omega_l(Q)$ (squares) and for the relaxation time $\tau(Q)$ (triangles). The slope of the line in Fig. 2 represents the expected hydrodynamic dispersion of sound modes with the adiabatic sound velocity $c_{ad}(\text{KCl}) = 1600\,\text{m/s}$ [17]. The derived $\omega_l(Q)$ values lie clearly above this line. We obtain a maximum of the phase velocity $c = \omega_l Q$ of 2350 m/s at $Q = 4.0\,\text{nm}^{-1}$, which corresponds to an increase of the velocity of 50%. There is a strong enhancement of the frequencies which indicates a more solid-like behavior in the probed THz range. From light Brillouin scattering measurements one can conclude that up to GHz frequencies no enhancement has occurred [16].

A higher propagation velocity with rising momentum transfers was observed in many liquids and is called *positive dispersion*. For example, in liquid alkali metals a positive dispersion of about 15–20% was observed. This enhancement in frequency has been related to a viscoelastic reaction of the liquid [20]. A transition from low frequency dynamics with viscous relaxation of the liquid to a high frequency elastic response describes the dynamics. At low frequencies the relaxations in the liquid can follow the density fluctuations and the sound waves propagate with the adiabatic sound velocity. For high frequencies the liquid can no more relax when the excitations pass by and the liquid response becomes solid-like. The acoustic modes propagate with a high frequency velocity $c_\infty(Q)$.

For monatomic systems the following ratio of the high frequency sound velocity c_∞ to the isothermal sound velocity c_T

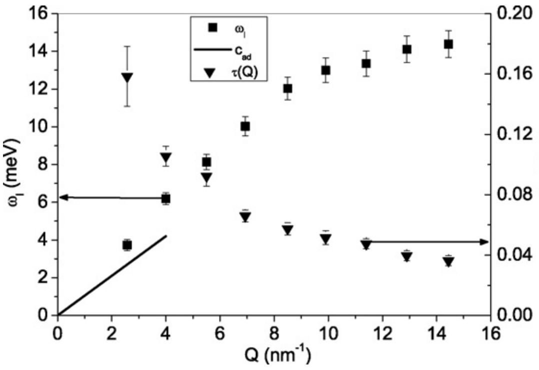

Fig. 2. Fit results are shown as squares for the excitation frequencies $\omega_l(Q)$. The relaxation time $\tau(Q)$ is plotted in addition (triangles). The adiabatic sound velocity of molten KCl is shown as a line.

was derived for the limit of small Q-vectors [20]:

$$\frac{c_\infty^2}{c_T^2} = 0.3\,\mathrm{nm}\,K_T\omega_E^2\sigma^2 \tag{3}$$

This ratio describes the enhancement of the frequencies and relates them to a macroscopic quantity, the isothermal compressibility K_T, and microscopic quantities, the hard core parameter σ and the Einstein frequency ω_E. We apply this equation to a binary liquid assuming that the similarity in masses will allow us to describe the particle density fluctuations alike as in a monatomic liquid. In Eq. (3) the isothermal compressibility $K_T = 38.4 \times 10^{-11}\,\mathrm{m^2/N}$ [17], the particle density $n = 2.4 \times 10^{22}\,\mathrm{cm^{-3}}$, the particle mass m, the Einstein frequency ω_E and the hard sphere parameter $\sigma = 3.1$ Å [17] appear. As the masses are very similar we use the average mass of both particles. The Einstein frequency is a mean oscillation frequency of a particle in its potential, which is nearly the center of gravity of the density of states. From a normal mode analysis of Ribeiro and Madden on molten alkali halides we deduce a value of $\omega_E \approx 10\,\mathrm{meV}$ for KCl [21]. From the adiabatic sound velocity we calculate the isothermal velocity $c_T = c_{ad}/\gamma = 1350\,\mathrm{m/s}$ with the specific heat ratio $\gamma = C_p/C_V = 1.4$ [17] for KCl. For $c_\infty = 2350\,\mathrm{m/s}$ we choose the largest measured phase velocity. Then, for the ratio of the velocities we get 3.03 and for the RHS of Eq. (3) we obtain 3.7. Although the agreement is not good, there is a trend that the frequency enhancement in molten salts could be understood as a viscoelastic reaction, as it was shown for many other liquids. This result was obtained by applying the formalism for the monatomic case. A more profound calculation for binary liquids using the fourth frequency moments, which are based on partial pair distribution functions and derivatives of the potential, is necessary to substantiate this conclusion.

From the fitted relaxation times $\tau(Q)$ we are able to extrapolate the viscosity. The damping of the sound modes is related to the quantity $(\omega_l^2 - \omega_0^2)\tau$ in the limit of small momentum transfers in the viscoelastic model. In hydrodynamics the damping of excitations is determined by the viscosity and thermal conductivity. Combining both under the assumption of negligible temperature fluctuations delivers the following relation [20]:

$$\tau = \frac{1}{\rho}\frac{(4/3)\eta_S + \eta_B}{c_\infty^2 - c_T^2} \tag{4}$$

From Fig. 2 we extrapolate $\tau = 0.2\,\mathrm{ps}$ in the limit $Q \rightarrow 0$. With the mass density ρ, the measured high frequency sound velocity $c_\infty = 2350\,\mathrm{m/s}$ and the isothermal velocity c_T we obtain a longitudinal viscosity $\eta_l = (4/3)\eta_S + \eta_B = 1.2\,\mathrm{mPa\,s}$. The shear viscosity, obtained from macroscopic methods, is $\eta_S = 1.38\,\mathrm{mPa\,s}$ and the bulk viscosity is $\eta_B = 24.0\,\mathrm{mPa\,s}$ [17]. Hence, this extrapolation fails by more than one order of magnitude to deliver the macroscopic viscosity value. To explain this failure, one could conclude that either the extrapolation from this microscopic model is not applicable or the bulk viscosity vanishes with rising Q-vector and only the shear viscosity remains for relaxation and damping of the modes on microscopic length scales. A similar large disagreement between microscopic and macroscopic viscosities was obtained by analyzing molten aluminium oxide data [22].

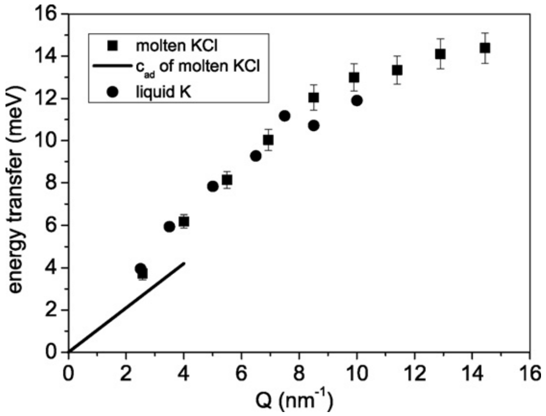

Fig. 3. The dispersion of molten KCl is plotted (squares) in combination with the dispersion of liquid potassium (circles) [23].

Although the acoustic-type dispersion in molten KCL seems to be describable within the viscoelastic model, in Fig. 3 we show a surprising experimental fact. The dispersion of the acoustic modes of molten KCl from the $\omega_l(Q)$ values is plotted combined with the dispersion of the liquid alkali metal potassium [23]. The liquid potassium data have been measured by neutron scattering and have been analyzed with a damped harmonic oscillator model. The agreement between both dispersions is astonishing. For liquid potassium a maximum phase velocity of 2360 ± 80 m/s was reported, a value which is within error bars of our results for molten KCl. A similar agreement we observed in a study on molten NaCl, where the dispersion of the salt is near to the dispersion of liquid sodium [18]. In NaCl the scattered radiation is also sensitive to charge density fluctuations, which can influence the dispersion at large Q-vectors. In KCl the synchrotron radiation is only sensitive to density fluctuations and rules out influences of high frequency optic-type modes as a reason for the shift to higher frequencies.

To get more insight we calculate current spectra $j(Q,\omega) = (\omega^2/Q^2)I(Q,\omega)$ from intensity spectra. Currents describe the flow of the particles and show always an inelastic peak, which is not necessarily related to a propagating mode. In Fig. 4 four current spectra are depicted. Clearly visible is the main inelastic peak which disperses with rising momentum transfer. This one is near to the observed ω_l dispersion in the spectra of $I(Q,\omega)$ and due to the multiplication with ω^2 shifted to larger frequencies. At small frequencies a second shoulder is observable, which shifts with rising Q, but less. Abramo et al. calculated partial dynamic structure factors within a memory function approach [24]. The calculations have been performed only for quite large Q-vectors and as input, data from a rigid-ion potential simulation have been used. They obtained partial current spectra for the different ions which look very similar to our measurements. Herein the low frequency shoulder already appears for a single ion and one would assign the two contributions in our measured current spectra always to both ion. A more recent MD-simulation on NaCl, based once more on a rigid-ion model and analyzed by the socalled generalized collective modes approach, concluded

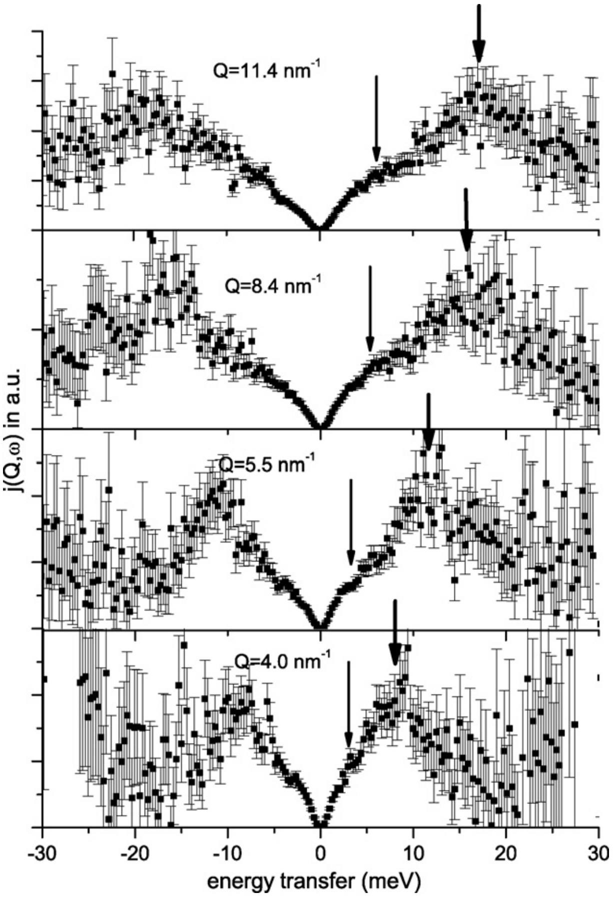

Fig. 4. Current spectra of four momentum transfers are shown. The thick arrows indicate the main inelastic peak and the thin arrows the shoulder at smaller frequencies.

that a separation of ion dynamics occurs for momentum transfers only beyond $Q = 17\,\mathrm{nm}^{-1}$[25]. With a larger mass difference this value moved to much smaller momentum transfers. These results indicate that a separation in ion dynamics at high frequencies does not occur at the exploited small momentum transfers.

All these simulation results have been obtained applying rigid-ion models. It has been demonstrated, that the polarizability of the ions influences the diffusive motion by an enhanced diffusivity of the cations [26], hence, one could suppose a distinct effect on the collective particle motion, too. The influence of polarization was already recognized long time ago in phonon studies on alkali halide crystals [10]. To explain the similarity in the dispersion relation between liquid KCl and liquid K one could speculate about a plasmon-type mode of the cations on a uniform anion background mediated by the polarized electron clouds of the anions. Whether inclusion of polarization would deliver a new picture on the high frequency collective ion dynamics is a question to MD-simulations with advanced potentials.

4. Conclusion

We measured the collective particle dynamics of molten potassium chloride with inelastic X-ray scattering. This composition is only sensitive to particle density fluctuations, which facilitates the analysis of the obtained spectra. We observed acoustic-type modes directly visible in the intensity spectra. A large positive dispersion was deduced from the data. The amount of frequency enhancement above the hydrodynamic expected values could be related within generalized hydrodynamics to a viscoelastic and therefore more solid-like behaviour of the molten salt at high frequencies. The extrapolated viscosity value is an order of magnitude smaller than the macroscopic value, which indicates a failure in the applicability of this model to extract macroscopic transport parameters. Surprisingly, the dispersion of the acoustic modes shows a strong similarity with the corresponding excitations in liquid potassium at high frequencies. This unexplained fact could suggest, that the high frequency sound mode might be understood as a plasmon-like motion of the cations on an anion background interfered by ion polarizability. A test from the experimental point of view could be to study a composition with strongly reduced influences of polarization, e.g. sodium fluoride.

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