X-ray scattering as a probe for warm dense mixtures and high-pressure miscibility

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Abstract – We develop a new theoretical approach that demonstrates the abilities of elastic X-ray scattering to yield thermodynamic, structural, and mixing properties of dense matter with multiple ion species. The novel decomposition of the electron structure factor in multi-component systems provides the basis to study dense mixtures as found in giant gas planets or during inertial confinement fusion. We show that the scattering signal differs significantly between single species, microscopic mixtures, and phase-separated fluids. Thus, these different phases can be distinguished experimentally via elastic X-ray scattering.

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Introduction. – Most materials in nature and technical applications consist of multiple atomic species and their properties can only be understood if all mutual interactions are fully considered. This fact is also true for high-energy-density matter in astrophysical objects and inertial confinement fusion experiments. Indeed, objects such as brown dwarfs, crusts of neutron stars, and giant planets can be considered as natural laboratories for the equation of state of dense, high-pressure mixtures [1–4]. Of special interest is in this context warm dense matter with densities similar to solids and temperatures of a few electronvolts. Matter with such parameters is in a partially ionized, fluid state with a well-pronounced short-range order within the ions subsystem. In this state, neither lattice symmetries as in solids nor the ideal mixing as in ideal plasmas can be employed.

Demixing and the subsequent segregation of the heavy elements can play a crucial role in the energy balance of planets [5]. Moreover, the assumed separation into helium-rich and helium-poor phases determines a layer boundary in gas planets like Jupiter and Saturn which has far-reaching implications on the interpretation of observed data [2,3] and our understanding of planetary formation. Phase separation in hydrogen-helium mixtures has been predicted by quantum simulation for conditions found in the interior of gas giants [6,7]. As a verification in astrophysical settings is quite indirect and requires full scale modeling of planets, laboratory experiments are needed to investigate these extreme conditions. Here, one may also study such complex, but very interesting processes as the formation of pure carbon from methane under the high pressures found in Neptune [8].

Driven by the progress in inertial confinement fusion [9–11], mixing of hot, shock-compressed materials receives currently also much interest. As the boundary between fuel and ablator is hydrodynamically unstable during the compression, fuel and shell material mix. The degree of mixing strongly affects the performance of fusion targets and can even prevent sufficient burn or ignition [12]. The experimental test of shell-fuel mixing under such extreme conditions proves to be very difficult. First results were inferred from the yield of fusion products during implosions of doped plastics shells which were diagnosed by charged-particle spectroscopy and X-ray images [13–18]. Whereas mixing could be described well in these studies, other spectroscopic investigations showed significant underestimated of mixing by theoretical models [19,20].

X-ray Thomson scattering has been shown to robustly deliver basic plasma parameters like density, temperature, and ion charge state as well as dynamic and structural properties of simple materials [21–23]. Here, one uses the fact that the experimental scattering spectrum from light...
elements has two distinct features: a frequency-shifted part related to the dynamically free electrons and an unshifted one (Rayleigh peak) due to elastic scattering from electrons that follow the ion motion [24]. Accordingly, the first feature gives the properties of the free electrons and the Rayleigh peak is related to the ion structure. Here, we will exploit the relation between the elastic Rayleigh peak and the ion structure and develop the theoretical framework for the application of elastic X-ray scattering as a new diagnostics to investigate mixtures and the high-pressure miscibility of multi-component systems.

First X-ray scattering experiments with two-component systems like plastics (CH) or lithium hydride (LiH) have already been performed [25–29]. Hitherto the theoretical description of the spectrum was however based on an ion structure that was generated from calculations for one-component plasmas via the relation [25]

\[ S_{ab}(k) = \delta_{ab} + \frac{\sqrt{n_a n_b}}{n} \frac{Z_a Z_b}{Z^2} \left[ S_{ii}^{1C}(k) - 1 \right]. \]  
(1)

Here, \( S_{ab} \) denote the partial ion structure factors, \( n_a \) and \( Z_a \) are the density and the charge of the ions of species \( a \). The structure for the effective one-component system, i.e. \( S_{ii}^{1C} \), is calculated using an average ion charge state defined by \( Z = \sum_a n_a Z_a / \sum n_a \). The description in relation (1) is only exact in the limit of weakly coupled plasmas where the random phase approximation (RPA) is applicable [30].

It is unable to describe the highly nonlinear effects in the structure of strongly coupled ions [31]. The application of X-ray scattering as a reliable diagnostic method for dense matter requires however a theoretical formalism that considers the full microscopic structure in the materials tested including the nonlinear interplay between different highly correlated ion species.

In this letter, we first derive the full multi-component description of the X-ray scattering signal. On this basis, we show that the elastic scattering feature is very sensitive to the ratio of species in the scattering volume. Therefore, it can be used as a probe for the degree of mixing in strongly compressed samples in the laboratory. Moreover, we predict considerable differences in the scattering spectra from microscopically mixed systems and matter that consists of two phases. The differences are particularly strong in hydrogen-helium mixtures under conditions found in the interior of Jupiter which demonstrates that elastic X-ray scattering can be applied to investigate demixing of hydrogen and helium under planetary conditions.

**Theoretical approach.** – We only briefly sketch our theoretical description of X-ray Thomson scattering that is developed along the ideas of Chihara [32,33] but it is here fully generalized to plasmas with multiple ion species. The influence of the ion structure is quite indirect as light is scattered by the electron density fluctuations. Therefore, the scattered intensity is proportional to the total electron structure factor \( S_{ee}^{\text{tot}}(k, \omega) \), where \( k \) and \( \omega \) are the wave number and frequency shifts of the photon, respectively [24]. This structure factor is the correlation function of electron density fluctuations

\[ S_{ee}^{\text{tot}}(k, \omega) = \langle g_{ee}^r(k, \omega) g_{ee}^{\text{tot}}(-k, 0) \rangle. \]  
(2)

Now we split the total electron density into a free part and contributions of core electrons associated with the \( N \) different ion species

\[ g_{ee}^{\text{tot}}(k, \omega) = \sum_{a=1}^N g_{ee}^a(k, \omega) + g^f(k, \omega). \]  
(3)

Applying this decomposition in the quadratic form of the total structure factor, we obtain \( N^2 \) bound-bound terms, \( N \) bound-free terms and one free-free term. All terms can be treated as in the case with just a single ion species. Core electrons belonging to different ions species \( \sum_{a \neq b} g_{ee}^a(k, \omega) g_{ee}^b(-k, 0) \) must however be treated carefully since this term defines a distinct ion-ion structure factor without core excitations.

Evaluating the different density correlations, we obtain for the total electron structure factor (in the following, the \( k \)-dependence is dropped for simplicity)

\[ S_{ee}^{\text{tot}}(\omega) = \tilde{Z} S_{ee}(\omega) + 2 \sum_a \sqrt{Z} x_a f_a S_{ea}(\omega) \]
\[ + \sum_a Z_a^c x_a \int d\omega' \tilde{S}_{ee}^{\text{tot}}(\omega' - \omega) S_{ea}^S(\omega') \]
\[ + \sum_{a,b} \sqrt{x_a x_b} f_a f_b S_{ab}(\omega). \]  
(4)

Here, we introduced the concentrations \( x_a = n_a / \sum n_a \), \( Z_a^c \) is the number of core electrons bound to ions of species with label \( a \). The first term describes correlations between two free electrons. The next term accounts for free-bound correlations where \( f_a \) is the atomic/ionic form factor of bound states of component \( a \). The second line contains self-contributions, i.e., internal excitations and bound-free transitions. Except the summation over all species, it is unchanged from its usual form. The last term describes correlations between two bound electrons.

The main problem using the expression (4) is the fact that all partial structure factors are inter-connected. This becomes particularly clear when considering \( S_{ee} \) which contains correlations between two screening clouds and, thus, also ionic properties. Indeed, the structure factors used in eq. (4) form a set of \( \frac{1}{2} N(N+1) \) equations [34]. This set can be conveniently written in matrix form and then inverted. Such a procedure yields

\[ \tilde{Z} S_{ea}(\omega) = x_a q_a S_{ea}(\omega) + \sum_{b \neq a} x_b q_b S_{ab}(\omega) \]  
(5)

for the free-bound structure factor. Here, \( S_{ab} \) denotes the partial ion-ion structure factors. The correlations of the
free electrons to the ions are contained in the screening function \(q_a(k)\) which are defined via

\[
g_a(k) = \frac{n_a C_{ee}(k) \chi_{ee}^0(k)}{1 - n_a C_{ee}(k) \chi_{ee}^0(k)},
\]

where \(C_{ee}\) and \(C_{ea}\) are the direct electron-electron and electron-ion correlation functions, respectively. In lowest order, these are given by the respective potentials. \(\chi_{ee}^0(k)\) denotes the density response of a free-electron gas [34].

For the free-free structure factor, one obtains

\[
\tilde{Z} S_{ee}(\omega) = \sum_{a,b} \sqrt{x_a x_b} q_a q_b S_{ab}(\omega) + S_{ee}^0(\omega),
\]

which now formally separates electron-ion correlations from the structure factor of the free-electron gas \(S_{ee}(k,\omega)\). The latter characterizes the kinetically free electrons in the system.

The results can be summarized in the total electron structure factor of the form

\[
S_{ee}^{tot}(\omega) = \sum_{a,b} \sqrt{x_a x_b} \left[ f_a + q_a \right] \left[ f_b + q_b \right] S_{ab}(\omega) + \tilde{Z} S_{ee}^0(\omega)
\]

\[
+ \sum_a Z_a^e x_a \int d\omega' \tilde{S}_{e\omega}^a(\omega - \omega') S_{e\omega}^0(\omega').
\]

The first term describes quasi-elastic scattering at bound electrons and the screening clouds associated to different ion species. In this contribution, the full ionic structure, expressed by the partial structure factors \(S_{ab}\), is required to interpret the scattering spectrum. As the ion motion cannot be resolved in current laser experiments, it is often sufficient to treat the partial structure factors statically: \(S_{ab}(k,\omega) = S_{ab}(k) \times \delta(\omega)\). The second term contains the full dynamic response of the free-electron gas which can, in lowest order, be described in RPA. Extensions include electron-ion collisions and local field corrections [35]. The last term describes contributions due to the excitation or ionization of bound electrons by X-rays.

**Results and discussion.** – The contributions due to inelastic X-ray scattering at free electrons, bound-free transitions, and internal excitations are unchanged from a description of matter with a single ion species [25]. Thus, we concentrate here on elastic scattering, that is the first term of eq. (8), which highlights mutual correlations between ions of different species. This contribution can also be extracted directly from experimental scattering signals as it is proportional to the area under the Rayleigh feature (the factor can be determined by calibration to either the free-electron feature or absolutely). Changes in the ion structure due to different concentrations, mixing or de-mixing are thus reflected in the elastic scattering feature and can be experimentally determined.

The dynamics of the ion motion contains a wealth of information [36]. However, the elastic part of the spectrum can often be treated statically as typical laser-driven X-ray sources and also current free-electron lasers have a bandwidth that cannot resolve the dynamics of the ion motion. In this case, the measured elastic scattering feature can fully be characterized by a single number: the area under the Rayleigh peak. Theoretically, this quantity is described by the weight of the Rayleigh peak

\[
W_R(k) = \sum_{a,b} \sqrt{x_a x_b} \left[ f_a(k) + q_a(k) \right] \left[ f_b(k) + q_b(k) \right] S_{ab}(k).
\]

To evaluate this expression, we use structure factors of fully interacting systems obtained from either quantum \textit{ab initio} simulations (DFT-MD) [37,38] or solutions of the hypernetted chain equations (HNC) [31]. The screening functions are used in linear response to a Coulomb field, \(q_a(k) = Z_a \kappa^2/\left(\kappa^2 + k^2\right)\) with the inverse electron screening length \(\kappa\) [39]. Note that the screening clouds are here \(Z\)-dependent whereas the method of ref. [25] only uses an averaged screening cloud. The form factors \(f_a\) are taken from isolated atoms/ions [40].

First we compare the full multi-component formula (8) and the approximate treatment of ref. [25] which is based on the structure of an average ion component via eq. (1). Both approaches agree for weakly coupled systems, but large differences occur for strongly coupled systems as shown in fig. 1 (\(\Gamma_i \approx 80\)). For both the screened and unscreened ion systems, the maximum of the Rayleigh peak is shifted resulting in more than 100% difference in the resulting scattering signal for \(k < 3 \text{ Å}^{-1}\) which allows for an experimental distinction between the theories. This small \(k\) behavior reflects the fact that the higher charged carbon ions imprint their structure onto the proton subsystem which cannot be described by the one-component calculation. The mutual screening of the ions is neglected in the reduced model which results in
The system is in pressure equilibrium with pure beryllium at 100%, 80%, 50%, 20%, and 0%. The temperature of the system also for systems that contain both materials in two pure phases.

The concentrations of beryllium are (from top to bottom): 100%, 80%, 50%, 20%, and 0%. The temperature of the system is \( T = 13 \text{ eV} \). The total densities were arranged in a way that the system is in pressure equilibrium with pure beryllium at \( n_{\text{Be}} = 3.707 \times 10^{23} \text{ cm}^{-3} \). The lower panel displays the related partial beryllium-beryllium structure factor. The grey shaded area and the two arrows indicate wave vectors used in recent experiments.

a strongly underestimated Rayleigh peak at small \( k \). The screened interactions are more realistic [23], but the results for unscreened ions demonstrate that the reduced model may predict even negative \( W_R \) (especially, for small \( k \)). For any strongly coupled, multi-component system, the analysis should thus be based on the new expression (8) to avoid unphysical behavior.

Let us now turn to the application of the new multi-component description for the mixing of beryllium and hydrogen as it occurs during inertial-fusion experiments. Due to the strong drive, the initially well-defined interface between the two materials experiences a Rayleigh-Taylor instability. At this stage, a volume element close to the original boundary will contain two fluids. However, these fluids consist of either pure beryllium or hydrogen and the system is made of two distinct phases. Later both materials will microscopically mix due to diffusion. Both hydrodynamic and microscopic mixture needs to be well understood to design fusion capsules with efficient burn.

Figure 2 demonstrates that the degree of mixing in dense beryllium-hydrogen systems can be investigated by measuring the strength of the elastic scattering feature. To allow for experimental verification, we have taken the conditions from a recent X-ray scattering experiment on pure, shock-compressed beryllium [41]. We have also used total densities as found in a situation behind a shock front. Here, all possible mixtures will be compressed until they are in pressure equilibrium with the driven beryllium. Thus, we have adjusted the total densities of the mixtures until the pressure matches the one of the pure beryllium. This procedure yields, e.g., a density of \( n_{\text{H}} = 8 \times 10^{22} \text{ cm}^{-3} \) for the case of 100% hydrogen.

As beryllium scatters more efficiently than hydrogen, the strength of the elastic (Rayleigh) feature is a strong function of the mixing ratio (beryllium content) in the scattering volume. This fact yields a clear experimental signal for beryllium-hydrogen mixing if the volume probed is close to the original boundary. Systems with a higher beryllium content also show a more pronounced maximum at intermediate wave numbers \( k \). This point can be traced back to the form of the ionic structure factors which have, with increasing beryllium concentration, an increasingly deeper correlation hole at small \( k \) values. Accordingly, they rise more strongly for intermediate \( k \). The different coupling strengths between the beryllium ions result from both the changes in the densities and the fact that the hydrogen (protons) lead to an additional contribution to the screening of the forces between the beryllium ions. As a result, the effective coupling strength and the structure in the beryllium subsystem is decreased with increasing hydrogen concentration.

Interestingly, both microscopic mixtures and two-phase systems scatter very similar at small \( k \). Here, the signal is mainly determined by the partial beryllium-beryllium structure factors and we can use these data to calculate the concentrations. However, significant differences of up to 60% arise in the weight of the Rayleigh peak for larger wave vectors. These differences can clearly exceed experimental uncertainties and allow for the experimental detection of phase-separated fluids and microscopic mixing.

We also want to mention that current laser-based X-ray sources allow for sufficiently high photon energies that can penetrate dense systems as in fig. 2 and have also enough flexibility to adjust the wave number to the appropriate value. Tested experimental platforms apply, e.g., titanium Ly-\( \alpha \), He-\( \alpha \), and K-\( \alpha \) lines [21,27], manganese He-\( \alpha \) and intercombination lines [41], chlorine Ly-\( \alpha \) lines [22,23], and copper K-\( \alpha \) lines [28]. Moreover, the scattering angle can be adjusted to change the wave number.

In the next example, we investigate a hydrogen-helium mixture under conditions similar to the interior of giant gas planets (\( x_{\text{He}} = n_{\text{He}}/(n_{\text{He}} + n_{\text{H}}) = 0.0756 \)). Density and temperature used in fig. 3 yield a system in the atomic/molecular phase (small ionization). In this case, the correct description of neutral as well as charged particles requires \textit{ab initio} simulations to determine the ionic structure. Figure 3 demonstrates that the weight of the elastic Rayleigh feature displays large differences between the pure substances and mixtures. These differences are
large enough to be observable in current experimental setups (see, e.g., [42]). Indeed, we find very distinct features for the different systems: pure helium scatters by far the most effective and displays a maximum around $k = 4\,\text{Å}^{-1}$, the mixture shows a monotonically decreasing shape, while $W_R(k)$ for pure hydrogen is almost featureless. Due to the mixing ratio, the two-phase system is dominated by the properties of hydrogen. In particular, we find huge differences between the microscopic mixture and systems consisting of two phases for small $k$ (up to a factor of five) which opens the possibility to study hydrogen-helium phase separation under the extreme planetary conditions found in Jupiter in the laboratory. Such experiments will require the combination of nearly isentropic compression and X-ray scattering which both have been demonstrated separately.

The reason for the large differences in the behavior of elastic scattering of pure helium, pure hydrogen and their mixtures lies not only in the fact that helium atoms scatter X-rays more efficiently. The different structure factors play also an important role. Pure helium has a strong peak in the structure factor which is also imprinted in the elastic scattering peak. This feature disappears in the mixture where the helium concentration is too low to be significant. Nevertheless, this small fraction mitigates the correlations within the hydrogen subsystem. Thus, small hydrogen-helium correlations lead to a shape of the function $W_R(k)$ that is dominated by the decreasing atomic form factor.

Similar results are also found for other conditions on Jupiter's isentrope. Figure 4 shows a hotter system as an example. Here, the hydrogen is ionized which requires to substitute the atomic form factor $f(k)$ by the form of the screening cloud $q(k)$. Again, the partial structure factors have been computed by quantum simulations (DFT-MD) [38]. Figure 4 shows that one can find a clear distinction between pure substances and hydrogen-helium mixtures for such hotter systems as well. Again, pure helium yields the most pronounced elastic scattering feature. However, the differences between a microscopic mixture and a two-phase system with separated elements is also within the reach of an experimental verification.

**Conclusions.** – We have derived a novel description for X-ray scattering in systems with multiple atomic or ion species that takes all correlations, in particular between different ion species, fully into account. The results show that X-ray scattering is a powerful tool to investigate dense mixtures and the mixing or demixing of materials
under extreme conditions as they occur during inertial
fusion experiments and in the interior of old stars and
giant gas planets. The conditions for the examples were
chosen to demonstrate that the proposed investigations
are feasible with present, well-tested setups on existing
high-energy laser facilities. More precisely defined X-ray
beams and a better time structure will become available
at the free-electron laser facilities LCLS and European
XFEL. This might further enhance the quality of the data
and allow for an unprecedented comparison of theoretical
predictions and X-ray scattering experiments.

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