Electron–ion structure factors and the general accuracy of linear response

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Abstract

We show that electron–ion structure factors in fluid metallic systems can be well understood from an application of *linear response* in the electron system, combined with hard-sphere-like correlation for the ionic component. In particular, we predict that electron–ion structure factors fall into two general classes, one for high ($Z > 3$) and one for low ($Z \leqslant 2$) valence metals, and make suggestions for experiments to test these ideas. In addition, we show how the general success of electronic linear response for most metallic systems stems in part from an intrinsic interference between atomic and electronic length scales which weakens the nonlinear response. The main exception to this is metallic hydrogen. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

At a near fundamental level, liquid metals are complex binary fluids consisting of ions in a sea of conduction electrons, their physical properties linked to the three corresponding correlation functions: $S_{II}(k)$, $S_{eI}(k)$, and $S_{ee}(k)$ [1]. We present a simple and evidently accurate analytic scheme to calculate electron–ion structure factors ($S_{eI}(k)$) by combining a hard-sphere approximation for the ionic structure with a simple linear response theory for the electrons. These structure factors are now in principle accessible experimentally through recent advances in both neutron and X-ray scattering techniques. Another route to effective electron–ion interactions therefore opens, but now through the fluid state.

We also address the evident success of the linear approximation by studying a related problem, the density, $\rho^{ind}(\vec{k})$, of an initially uniform electron gas induced by an embedded pseudo-potential, $v^{ps}(\vec{k})$. By comparing linear and second order response to full (Kohn–Sham [2]) nonlinear response, we show that even though $v^{ps}(\vec{k})$ is not necessarily a small perturbation, the consequent response series converges term by term. The nonlinear terms are significantly reduced by an interference between atomic and electronic length scales for most metals, the main exception to this being hydrogen.

2. Discussion

2.1. Electron–ion correlation functions

The electron–ion-structure factor can be written [1] as:

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$$S_{eI}(k) = \frac{1}{\sqrt{N_e N_I}} \langle \hat{\rho}_e^{(1)}(\mathbf{k}) \hat{\rho}_I^{(1)}(\mathbf{k}) \rangle = \frac{n(k)}{\sqrt{Z}} S_{II}(k), \qquad (1)$$

where $\hat{\rho}_j^{(1)}(\mathbf{k})$ is the Fourier transform of the one-particle density operator of component j, $S_{II}(k)$ is the ion–ion structure factor and $n(k)$ is identified as the pseudo-electron density, or pseudo-atom (of valence Z). Thus electron–ion correlations can be described by convolving the pseudo-atom with the ionic correlations. The ionic correlations are themselves well described by a Percus–Yevick hard-sphere structure factor [3], while the pseudo-

atom is described by a standard linear response formulation:

$$n(k) = \chi_1(k) v^{ps}(k), \qquad (2)$$

where $\chi_1(k)$ is the well-known linear response function; to approximate $\chi_1(k)$ we use a Local Density Approximation (LDA) local field factor [4]. The electron–ion interaction is modeled by a simple local one-parameter empty-core pseudo-potential [5] i.e.: $v^{ps}(k) = -(4\pi e^2/k^2)\cos(kR_c)$, where R_c is the core radius and the pseudo-potential goes through zero at $k_0 = \pi/2R_c$. (We
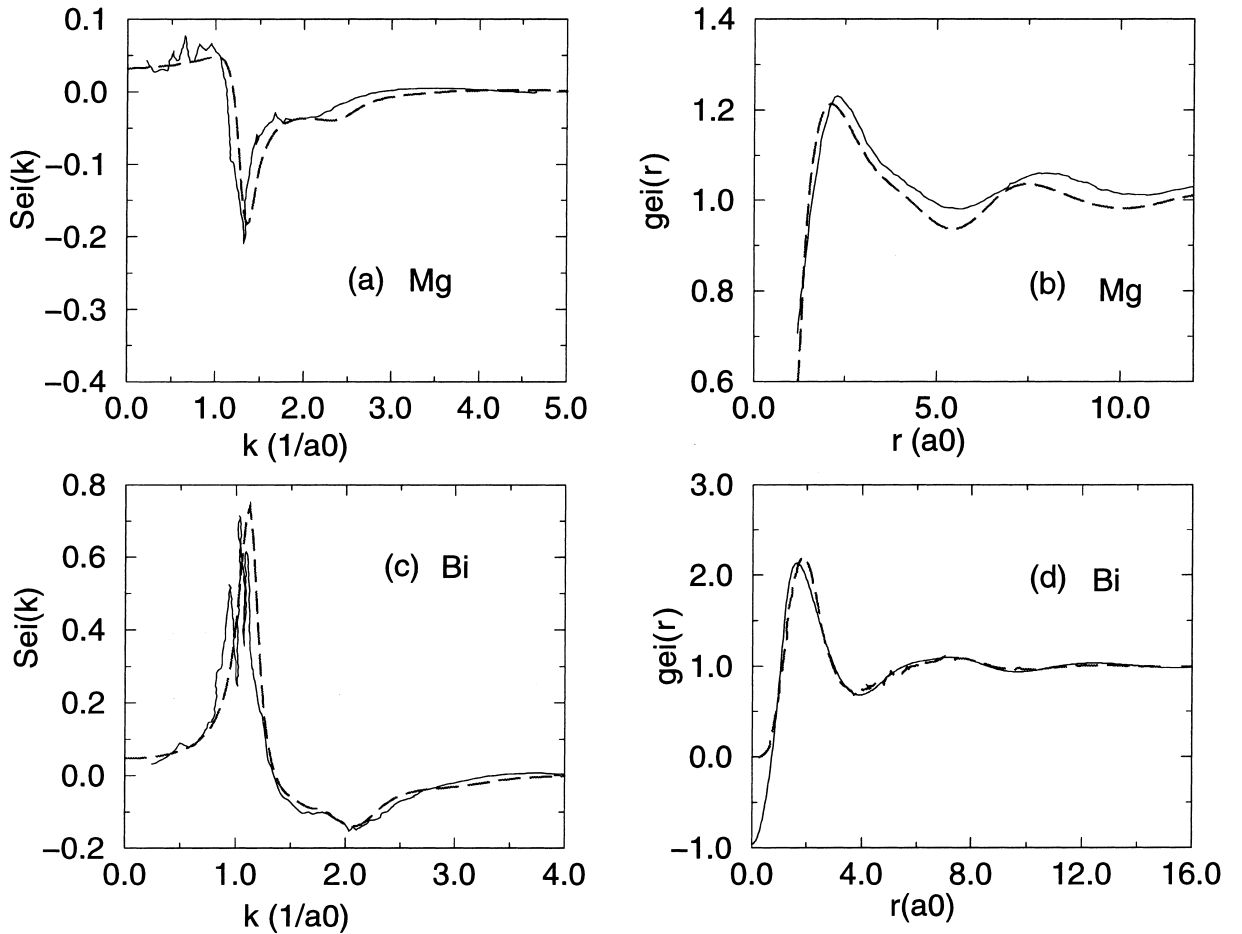

Fig. 1. The electron–ion structure factors $S_{eI}(k)$ and related electron–ion correlation functions $g_{ei}(r)$ for Mg and Bi: Car–Parrinello results of de Wijs et al. [8] (solid line) vs. the simple linear-response approach augmented by a hard-sphere approximation (dashed line). Panel (a) shows $S_{eI}(k)$ and panel (b) shows $g_{ei}(r)$ for liquid Mg. Panel (c) shows $S_{eI}(k)$ and panel (d) shows $g_{ei}(r)$ for liquid Bi. For Mg the parameters (taken from the literature) are: $r_s = 2.66a_0$, $R_c = 1.31a_0$ and for Bi the parameters (taken from the literature) are: $r_s = 2.25a_0$ and $R_c = 1.15a_0$. Both have a hard-sphere parameter, $\eta = 0.46$ (note that for the $g_{ei}(r)$ the region inside the core radius is not physically significant).

note that at this linear level, the effects of ionic averaging on the pseudo-atom are ignored [6].) Using the approximations above in Eq. (1), we compare our approach in Fig. 1 to the *full ab-initio* Car–Parrinello [7] calculations of de Wijs et al. [8]. The correspondence is striking, especially when we note that the parameters η and R_c are a priori set by other physical properties (no fitting is necessary).

Besides a semi-quantitative description of electron–ion structure factors, this linear response theory now provides an important qualitative insight into the form of the electron–ion structure factors [9]. The pseudo-atom density, $n(k)$, is typically largest for smaller k and thereafter rapidly declines for larger k, while the near classical ion–ion structure factor, $S_{II}(k)$, follows an inverse behavior; it is small for small k. Together with the product form (1) this implies that the shape of the electron–ion structure factor, $S_{eI}(k)$, is determined primarily by the the position of the *zero-crossing*, $\bar{k}_0$, of $n(k)$ with respect to the *first maximum*, k_p, of $S_{II}(k)$. If $\bar{k}_0 < k_p$, then $S_{II}(k)$ selects (or filters) the negative part of $n(k)$ and $S_{eI}(k)$ takes a form similar to that of Mg (Fig. 1(a)). Conversely, if $\bar{k}_0 > k_p$, then the ion–ion structure factor selects (or filters) the positive part of $n(k)$, and again, $S_{eI}(k)$ takes a form similar to that of Bi (Fig. 1 (c)). Since $\chi_1(k)$ is positive definite, the zero-crossing in linear response occurs at k_0. The large slope of $n(k)$ near the zero-crossing then implies that nonlinear corrections *must* have a small effect on the location of the zero-crossing, and this, together with the expected accuracy of linear response, implies that $\bar{k}_0 \sim k_0$. For most metals, k_0 is just a little less than $2k_F$, and the latter's ratio to k_p is well known: for low valence $(Z \leqslant 2)$, $2k_F < k_p$; for high valence $(Z \geqslant 3)$: $2k_F > k_p$ [10]. This accounts in a straightforward way for the two separate forms found by de Wijs et al. [8]: For Mg, $\bar{k}_0 < k_p$ $(Z = 2)$, which belongs to the *low valence class* of electron–ion structure factors. For Bi, $\bar{k}_0 > k_p$ $(Z = 5)$ and we may refer to this as the *high valence class* of electron–ion structure factors [11]. Generally ions of valence $Z \leqslant 2$ belong to the low valence class while ions with valence $Z > 3$ belong to the high valence class. Ions with valence $Z = 3$ typically belong to the high valence class also,

although they may be characterized by a crossover form [6]. The analytical approach above can easily be extended by using the modern theory of classical liquids to obtain improved ion–ion structure factors [12], but to include second order contributions to the pseudo-atom $n(k)$ necessitates not only second order electron response, but also contributions from ion–ion triplet structure. The latter can be carried out with concepts from the theory of classical liquids [6].

2.2. Proposed experiments

The principal features of electron–ion structure factors can be measured by exploiting the differences between the X-ray scattering structure factor, $S_{II}^X(k)$, determined with a free-atom form factor, $f_A(k)$, and the structure factor, $S_{II}^N(k)$, determined by neutron scattering [13,14]. As emphasized by Chihara [14] the X-ray structure factor for liquid metals will equal $S_{II}^N(k)$ only when determined with an ionic form factor augmented by a pseudo-atom form factor; i.e. $f_I(k) + n(k)$, so that:

$$\frac{S_{II}^X(k)}{S_{II}^N(k)} = \frac{|f_I(k) + n(k)|^2}{|f_A(k)|^2}. \tag{3}$$

This effect is clearly expected to be largest for metals with larger ratios of valence to core electrons. Thus we predict a small effect for metals with smaller valence to core ratio such as Na or K, a 2% difference at the 1st peak of the structure for Li (ratio = 1:2) or Al (ratio = 3:10), but by far the largest effect for Be (ratio = 1:1) where the difference at the principal peak of the structure factor could be as high as 7%, well within experimental range. Another interesting candidate would be metallic Si (ratio = 4:10) since covalent effects still make themselves felt in the liquid state suggesting that experiments could reveal effects beyond linear response.

To date the experimental electron–ion structure factors and related pseudo-atoms show considerably more structure than indicated by theoretical predictions [15]. Significant experimental challenges are faced in the accuracy resulting from subtraction of two sets of data obtained by quite different means, each with important (but

different) systematic corrections; however the present approach suggests that the current differences between X-ray and neutron scattering should be reexamined (see also Ref. [14]). Using a pseudo-atom instead of the full free atom as a form factor can assist in comparing neutron and X-ray measurements and help unravel various systematic corrections applied. The advent of high precision X-ray and neutron sources currently coming on-line suggests that these proposed effects can be systematically explored.

2.3. Nonlinear response of an atom in an electron gas

The evident (and long-standing) success of the linear response approximation for electron response [4], here demonstrated for electron–ion structure factors, calls for further investigation. The accuracy of linear response in a crystalline solid is commonly attributed to the fact that the structure dependent reciprocal lattice vectors are typically near the pseudo-potential zero-crossing, k_0, with the associated inference that the net scattering is smaller than one would naively expect [4]. For liquids or other disordered systems such arguments are less appropriate. To examine the strength of linear response in the absence of ionic structure, we consider a simpler problem, namely the response of the interacting electron gas to a single ion, where the electron–ion interaction is modeled by a simple local one-parameter empty-core pseudo-potential [5]. We will compare two routes to the induced density, $\rho^{\text{ind}}(k)$. The first follows from solving the Kohn–Sham equations [2] exactly (for the given pseudo-potential) within the LDA, the second from the standard expansion of the response in powers of the perturbing (pseudo) potential, i.e.;

$$
\rho^{\text{ind}}(k) = \chi_1(k) v^{\text{ps}}(k) \\
+ \sum_{\vec{k}_1} \sum_{\vec{k}_2} \chi_2(k, k_1, k_2) v^{\text{ps}}(k_1) v^{\text{ps}}(k_2) + \cdots .
$$

$$(4)$$

Here the response functions, $\chi_n(k_1 \ldots)$, are properties of the *homogeneous* interacting electron gas. In Fig. 2 we compare the explicit second order

response with an LDA local field factor [6,16] to the full nonlinear LDA response. Clearly the nonlinear response is well characterized by the second order term, implying that the success of linear response is not due to cancellation between higher order terms of opposite sign but instead that each successive term is individually small compared to the previous term in the expansion; *the response series converges very rapidly*, *term by term*.

The nonlinear response is largest for atomic parameter $R_c = 0$ (hydrogen), and decreases with a larger atomic-parameter, R_c, as might be physically anticipated. However as R_c increases from zero, a noticeable secondary minimum occurs when the inverse atomic length, k_0, is equal to $2k_F$. For the cases plotted in Fig. 2, the maximum in second order response at $k_0/2k_F = 1$ (or
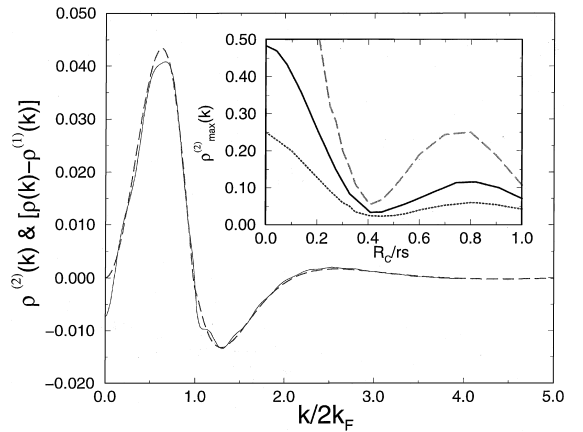

Fig. 2. A comparison of full nonlinear LDA response $[\rho(k) - \rho^{(1)}(k)]$ (solid line) to second order LDA response (dashed line) for an empty core pseudo-potential with $R_c = 1.5a_0$ embedded in an electron gas with density parameter, $r_s = 3a_0$. For the scale, compare this to the full response with the limit $\rho(k \to 0) = 1$. The higher order response is of the order of a few % of the full response and in turn, the second order response captures almost all the nonlinear response. (The small difference at $k \to 0$ is a numerical artifact stemming from the use of a large but finite real-space cut-off radius in the Kohn–Sham procedure.) In the insert is plotted the maximum of the second order response vs. R_c/r_s for $r_s = 2a_0$ (dotted), $r_s = 3a_0$ (solid) and $r_s = 5a_0$ (dashed). Note especially the minimum at $R_c/r_s = 0.41$ which corresponds to $k_0 = 2k_F$. It is reduced by an order of magnitude from the value at $R_c = 0$ (hydrogen) and is traced to an interference between atomic and electronic length-scales.

$R_c/r_s = 0.41$) is reduced by an entire *order of magnitude* when compared with the maximum in second order response calculated for hydrogen ($R_c/r_s = 0$), and is typically equal to the value at $3R_c/r_s$. The physics behind this minimum is attributed to the following; the second order response function, $\chi_2(k, k_1, k_2)$, peaks when the summed arguments in Eq. (4) are close to $2k_F$ [6]. If the pseudo-potential zero-crossing, k_0, is near the response peaks at $2k_F$, a maximal cancellation or *maximal destructive interference of the atomic and electronic length scales* occurs, leading to a minimum in second order response. The ratio of the atomic and electronic length scales is set primarily by the volume energy terms in the total ground state energy, and is almost independent of structure [4]; $k_0/2k_F$ lies between 0.75 and 1 for most metals, and is therefore very close to the secondary minimum in the nonlinear response.

As noted, the effect we discuss originates from an *interference* between intrinsic *atomic* and *electronic* length scales, but it also complements the argument given for crystalline solids alone, which stems from the *confluence* of an *atomic* and a *structural* length scale. The clear exception to these interference effects is again the singular case of a point-charge ($v^{ps}(k) \sim 4\pi e^2/k^2$), i.e. the case of hydrogen, which has no well-defined core-length scale, k_0, no oscillations in the potential and thus no interference effect in the higher order terms. In contrast to other systems, nonlinear response terms are large term by term. In fact, the response series may not even formally converge and care must be taken when applying concepts derived from linear-response theory to hydrogen (it is not a simple material).

Finally we note that the second order response contribution is of the same order as the difference between first order response with or without local field corrections. In addition, the combined effects of exchange and correlation partially cancel between first and second order, implying that *neglect of higher order response results in an over-estimation of the role of exchange and correlation*, which, in turn, has important implications for the widespread application of linear response theory in the derivation of effective ion–ion potentials in (simple) metals.

3. Conclusions

The electron–ion structure factors of liquid simple-metals are well described by a simple linear response theory augmented by linear response for the electrons. This approach suggests two main classes of electron–ion correlation functions, one for high and one for low valence metals. Experimental advances in X-ray and neutron-scattering may be able to provide measurements of these electron–ion correlation functions, with liquid Be being the most promising candidate. A route to information on fundamental electron–ion interactions therefore becomes available through the fluid state. Finally, the well-documented success of the linear response approximation for electrons stems in part from an interference effect between atomic and electronic length scales.

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