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## Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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**To cite this Article** Chushak, Ya. , Hafner, J. and Kahl, G.(1995) 'Dynamical Properties of the Liquid Polyvalent Elements: Soft Modes in Liquids', *Physics and Chemistry of Liquids*, 29: 3, 159 — 168

**To link to this Article:** DOI: 10.1080/00319109508028422

**URL:** <http://dx.doi.org/10.1080/00319109508028422>

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# DYNAMICAL PROPERTIES OF THE LIQUID POLYVALENT ELEMENTS: SOFT MODES IN LIQUIDS

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(Received 1, October 1994)

We present investigations of the dynamical properties of liquid polyvalent metals and semimetals (with liquid Ge and As chosen as examples). The static liquid structure is calculated via molecular dynamics, based on exact interatomic forces from pseudopotential perturbation theory. The dynamical structure factor is calculated in a viscoelastic approximation. The static structure factor  $S(k)$  of the polyvalent elements is characterized by a side-peak or shoulder to the main peak at  $k = Q_p$ . The side-peak is situated at  $k = 2k_F$  where  $k_F$  is the Fermi wavenumber. This shows that the structural anomaly is of electronic origin and may be interpreted in terms of a Peierls-like modulation of the packing of the atoms by the Friedel-oscillations in the interatomic forces. We demonstrate that the electronic effects also modify the dynamical structure factor and the dispersion relations of collective excitations and induce a mode-softening analogous to a Kohn-anomaly.

## 1 INTRODUCTION

During the past decade considerable effort has been devoted to the experimental<sup>1</sup> and theoretical<sup>2</sup> investigation of the dynamical properties of liquid metals. However most of the published results are concerned with the properties of the monovalent liquid alkali metals. For this class of materials, both the single-particle and the collective dynamics and their variation with temperature and density are now rather well understood<sup>2,3</sup>. In particular it has been demonstrated that for these metals the dispersion relation for collective propagating excitations may be followed up to rather high wavenumbers. At small  $k$  the dispersion relation is essentially linear, with a slope determined by the adiabatic velocity of sound. At larger  $k$  the dispersion curve bends over and goes through a maximum at  $Q_p/2$  and then through a minimum at  $Q_p$  where  $Q_p$  is the wavenumber where the static structure factor  $S(k)$  has its main peak. The origin of the dispersion minimum is essentially in a “diffuse Umklappscattering” process<sup>4,5</sup>: the relatively sharp peak in  $S(k)$  acts like a smeared-out Bragg peak, and in some sense the region  $0 \leq k \leq Q_p/2$  represents something like a “pseudo-Brillouinzone”. It has also been recognized that the existence of

well-defined collective excitations depends on the nature of the interatomic forces: the softness of the interatomic potentials in the heavy alkali metals is essential for avoiding the overdamping of the collective excitations in the region around  $Q_p$  that is characteristic for hard-sphere and Lennard-Jones liquids<sup>6,7</sup>.

Relatively little is known about the dynamical properties of the liquid polyvalent elements. The most significant results have been obtained in the work of Larsson, Dahlborg and coworkers<sup>8-12</sup> on liquid Pb and Bi. Liquid Pb is a good metal, whereas liquid Bi already shows some semimetallic properties. The difference in the chemical bonding forces leads to a weak structural anomaly in liquid Bi (a broad shoulder at the foot of the right-hand side of the main peak) and some small differences in the dynamical structure factor  $S(k, \omega)$  as well.

The differences in the liquid (and crystalline) structures of Pb and Bi are just a small example of general trends in the structures of the B-group elements<sup>13</sup>: (i) Within each row of the Periodic Table we find a transition from close-packed metallic structures with high coordination numbers to open covalent structures with low coordination numbers, most distinctly expressed in the series Al( $N_c^s = N_c^l = 12$ ) – Si( $N_c^s = 4, N_c^l = 6.5$ ) – P( $N_c^s = N_c^l = 3$ ). (ii) Within group III we find first a transition from a close-packed structure in Al to a more open structure in Ga ( $N_c^s = 7, N_c^l = 10$ ), but then a return to more metallic structures in In and Tl. (iii) The transition to more metallic structures with increasing atomic number also dominates in groups IV (Si – Ge – Sn – Pb) and V (P – As – Sb – Bi). It has been shown that the structural trends may be explained qualitatively for the crystalline phases<sup>13</sup> and quantitatively for the liquid phases<sup>14-17</sup> in terms of the variation of the interatomic potentials with the atomic volume, the electron density and the ionic pseudopotential. Detailed molecular dynamics simulations and X-ray and neutron diffraction experiments show that the liquid structure of the molten semiconductors (Si, Ge, P) and semimetals (As, Sb, Bi) are characterized by a side-peak at the right-hand side of the main peak situated at  $k = 2k_F$  where  $k_F$  is the Fermi-wavenumber. The dependence on the Fermi-wavenumber proves that this structural feature is electronically induced and it has been shown that it arises from the modulation of the atomic geometry by the Friedel-oscillations in the interatomic potential. It has also been argued that this “Friedel modulation” is just the correct real-space description of a Peierls distortion in a disordered material<sup>15,17</sup>. Both the amplitude of the Friedel oscillations and the Peierls-gap in the electronic spectrum are set by the on-Fermi-surface matrix-elements  $\omega(2k_F)$  of the screened ionic pseudopotential.

The results of Dahlborg *et al.*, for Pb and Bi suggest that this may also be the physical mechanism that causes the differences in the dynamical properties of Pb and Bi (which are, however, quite small). It is therefore of interest to examine the dynamical properties of elements where the structural effects are more pronounced and where we can expect to find a significant effect in the dynamical properties as well. This is precisely the aim of the present study. We present a calculation of the dynamical properties of liquid Ge and As, based on results for the static structure from molecular dynamics simulations and a simple viscoelastic approximation<sup>18,19</sup>. The viscoelastic approximation should be sufficiently reliable for an exploratory study (as has been shown recently for the case of some alkali metals<sup>20</sup>); Ge and As have been chosen as examples because for these elements the description of the

structure in terms of pseudopotential-derived interatomic forces<sup>21</sup> agrees well with experiment and has also been confirmed by sophisticated *ab-initio* molecular dynamics simulations based on the full set of quantum-many-body forces<sup>22-24</sup>. We show that the electronic effects that induce the structural anomalies in l-Ge and l-As also lead to a softening of the modes with wavevectors close to the diameter of the Fermi-sphere, through the same mechanism that leads to the appearance of Kohn-anomalies in the phonon-dispersion relations of crystalline metals.

## 2 DYNAMICAL STRUCTURE FACTOR IN THE VISCOELASTIC APPROXIMATION

In the viscoelastic approximation the dynamical structure factor  $S(k, \omega)$  is given by<sup>18,19</sup>

$$S(k, \omega) = \frac{1}{\pi} \frac{\tau(k) \omega_0^2(k) [\omega_l^2(k) - \omega_0^2(k)/S(k)]}{[\omega \tau(k) (\omega^2 - \omega_l^2(k))]^2 + [\omega^2 - \omega_0^2(k)/S(k)]^2} \quad (1)$$

where  $\tau(k)$  is a relaxation time, given in the approximation of Lovesey<sup>25</sup> by

$$\frac{1}{\tau(k)} = \frac{2}{\sqrt{\pi}} [\omega_l^2(k) - \omega_0^2(k)/S(k)]^{1/2}. \quad (2)$$

The characteristic frequencies  $\omega_0(k)$  and  $\omega_l(k)$  may be expressed in terms of the moments of the dynamical structure factor as

$$\omega_0^2(k) = \int_{-\infty}^{\infty} \omega^2 S(k, \omega) d\omega = v_{\text{th}}^2 k^2 \quad (3)$$

where  $v_{\text{th}} = \sqrt{k_B T/m}$  is the thermal velocity and  $m$  the mass of the ions, and

$$\omega_0^2(k) \omega_l^2(k) = \int_{-\infty}^{\infty} \omega^4 S(k, \omega) d\omega \quad (4)$$

with  $\omega_l(k)$  expressed in terms of the pair correlation function  $g(r)$  and the interatomic potential  $V(r)$  as

$$\omega_l^2(k) = 3\omega_0^2(k) + \frac{n}{m} \int g(r) (1 - \cos kz) \frac{\partial^2 V(r)}{\partial z^2} d^3r. \quad (5)$$

where  $n$  is the number density.

Upper and lower bounds for the dispersion relation  $\omega = \omega_m(k)$  of propagating collective excitation are given by  $[\omega_0(k)/\sqrt{S(k)}]$  and  $\omega_l(k)$ , i.e.  $[\omega_0(k)/\sqrt{S(k)}] \leq \omega_m(k) \leq \omega_l(k)$  where  $\omega_m(k)$  is defined in terms of the maximum of the longitudinal current correlation function  $C_l(k, \omega) = (\omega^2/k^2) S(k, \omega)$ .

The quantity  $[\omega_l^2(k) - 3\omega_0^2(k)]$  appearing in Eq. (5) can be separated into the Einstein frequency

$$\Omega_0^2 = \frac{n}{m} \int g(r) \frac{\partial^2 V(r)}{\partial z^2} d^3r \quad (6)$$

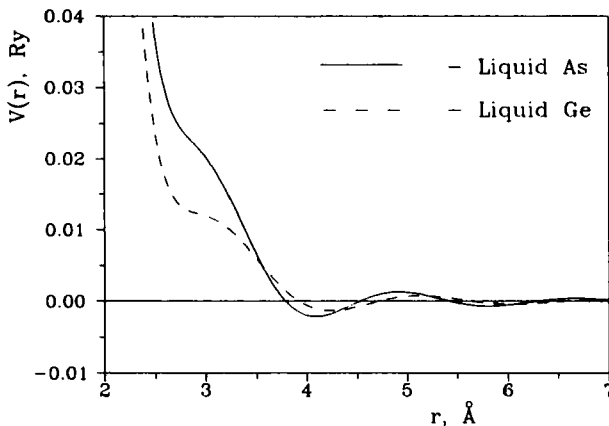
of the system and an oscillatory term

$$\Omega_l^2(k) = \frac{n}{m} \int g(r) \cos kz \frac{\partial^2 V(r)}{\partial z^2} d^3r. \quad (7)$$

The viscoelastic approximation should give a semiquantitatively accurate representation of the dynamical structure factor in the  $(k, \omega)$ -range accessible to neutron-scattering investigation in combination with a mode-coupling analysis<sup>26</sup> of the simulation data.

### 3 RESULTS: ELECTRONICALLY-INDUCED SOFT COLLECTIVE MODES IN LIQUIDS

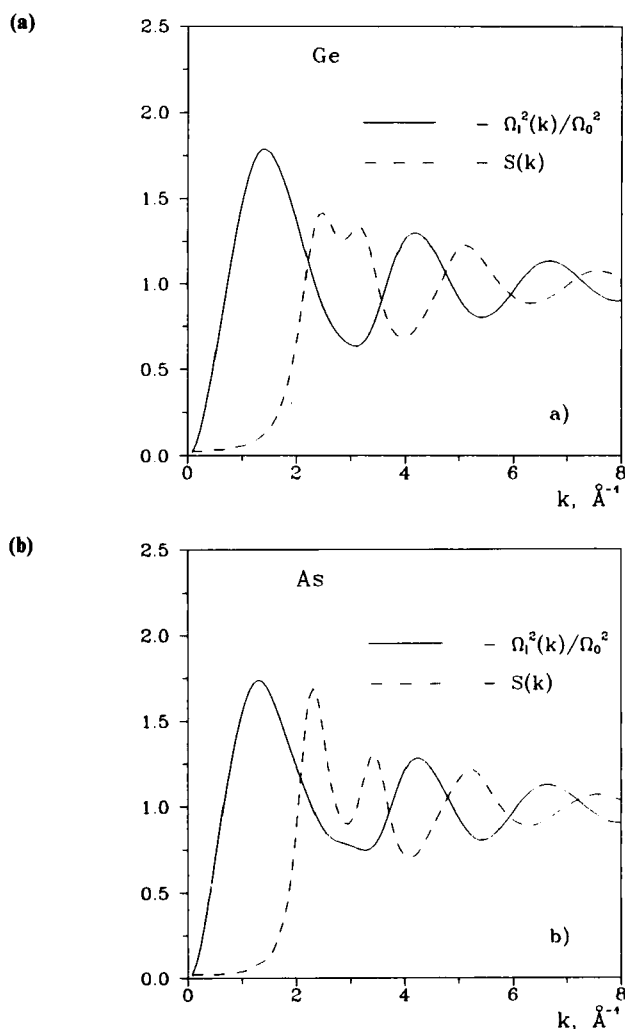
Our investigations refer to liquid germanium at a temperature of  $T = 1250$  K and a density of  $\rho = 5.56 \text{ gcm}^{-3}$  and liquid arsenic at  $T = 1103$  K and  $\rho = 6.08 \text{ gcm}^{-3}$ . The interatomic potentials have been calculated with a simple local empty-core model potential<sup>27</sup> with core-radii of  $R_c = 0.545 \text{ \AA}$  for Ge and  $R_c = 0.53 \text{ \AA}$  for As, and using the dielectric screening functions with the local-field corrections proposed by Ichimaru and Utsumi<sup>28</sup>. The potentials are shown in Figure 1. The characteristic feature is that with increasing electron density, the repulsive part of the potential begins to cover the first attractive minimum close to the nearest neighbour distance for close-packing: remember that the equilibrium density is determined by the equilibrium



**Figure 1** Interatomic pair-potential  $V(r)$  for liquid Ge (dashed line) and liquid As (full line).

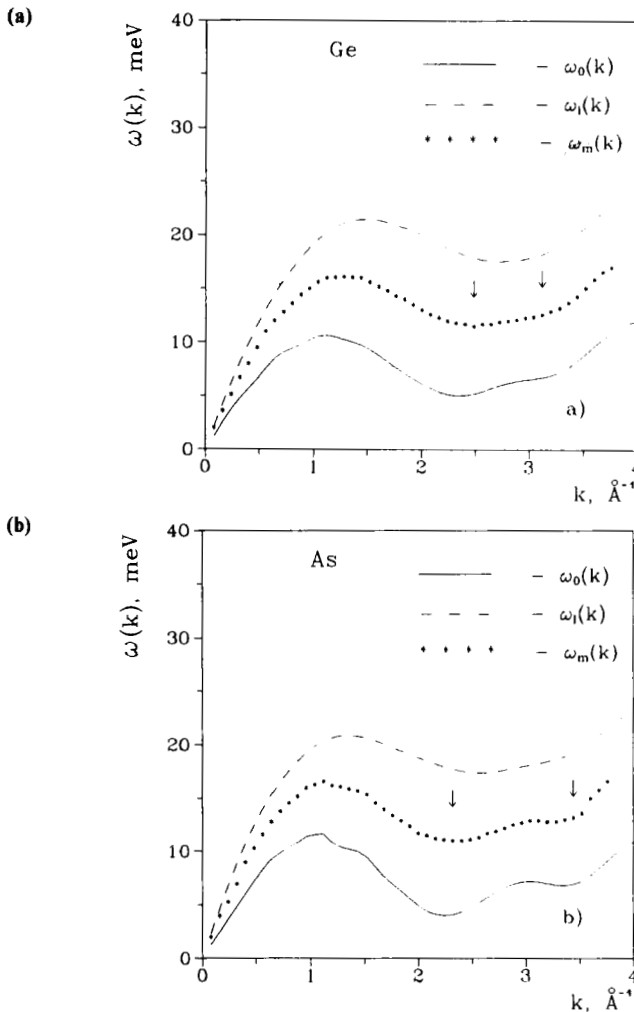
between the pair- and volume-forces giving contributions of opposite sign to the internal pressure. The trends in the interatomic forces have been discussed in detail by Hafner and Heine<sup>13</sup> and detailed calculations using integral-equation techniques<sup>14</sup> and molecular-dynamics simulations<sup>29,15-17</sup> have shown that even with simple model potentials an almost perfect fit to the measured static structure factors of the polyvalent liquid metals and semimetals may be achieved. The validity of the pair-potential approximation has also been confirmed by *ab-initio* calculations based on the full set of quantum-many-body forces<sup>22-24</sup>.

The Einstein frequencies calculated for liquid Ge and As are  $\hbar\Omega_0 = 15.33$  meV (Ge) and  $\hbar\Omega_0 = 15.38$  meV (As). Figures 2(a,b) show the ratio  $\Omega_l^2(k)/\Omega_0^2$ , compared with the



**Figure 2** The ratio  $\Omega_l^2(k)/\Omega_0^2$  (full line) compared with the static structure factor  $S(k)$  for liquid Ge (a) and As (b).

static structure factor: quite generally a peak in  $S(k)$  induces a minimum in the characteristic frequencies for propagating collective excitations. For Ge and As both the principal peak at  $k = Q_p$  and the side-peak at  $k = 2k_F$  in  $S(q)$  fit into the first dispersion minimum so that the second dispersion maximum appears at a larger wavenumber than corresponding to a simple 'pseudo-Brillouin-zone' structure. That the structure of collective excitations is influenced by electronic effects is also evident from the dispersion relations defined in terms of the position  $\omega_m(k)$  of the maximum in the longitudinal current correlation function  $C_l(k, \omega)$  and the upper and lower bounds  $\omega_0(k)$  and  $\omega_l(k)$  defined in Eqns. (3, 5). For liquid As (Fig. 3(b)) we find a

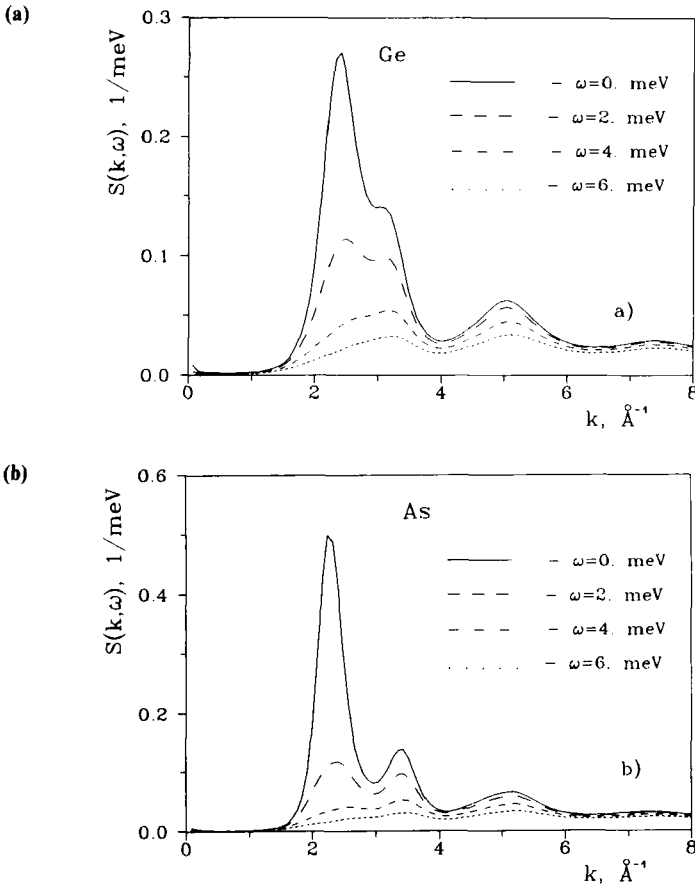


**Figure 3** Dispersion relation  $\omega_m(k)$  (asterisks), and upper and lower bounds  $\omega_0(k)$  (full line) and  $\omega_l(k)$  (dashed line) to the eigenfrequencies of collective excitations for liquid Ge (a) and As (b). The vertical arrows indicate the positions  $Q_p$  of the main peak in the static structure factor and the diameter  $2k_F$  of the Fermi sphere (cf. text).

double minimum in  $\omega_m(k)$  at  $k = Q_p$  and  $k = 2k_F$ , for liquid Ge (Fig. 3(a)) at least an inflection at  $k_F$  is visible in the dispersion relation. Hence the electronic effects lead to a softening of the eigenfrequencies of propagating collective modes with wavevectors close to the diameter of the Fermi-sphere.

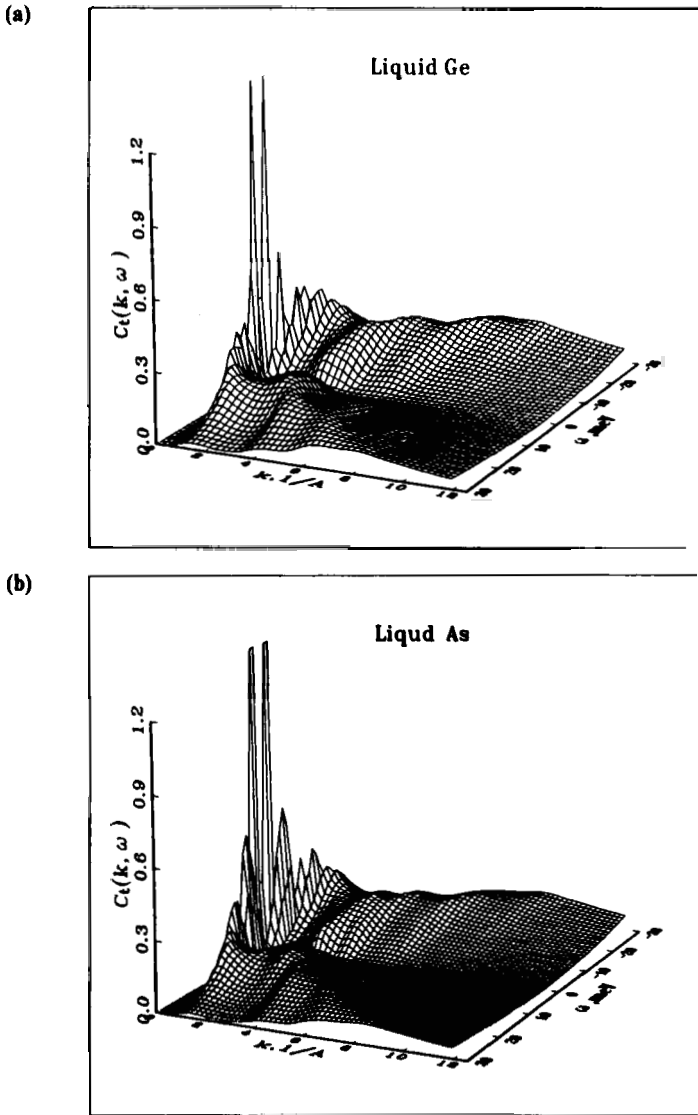
The importance of the electronically induced effects is also evident from the dynamical structure factor  $S(k, \omega)$  (Figs. 4(a, b)): in the limit  $\omega \rightarrow 0$  one finds the characteristic double-peak at  $k = (Q_p/2)$  (resulting from the packing effects, since  $Q_p \sim 2\pi/D_{\text{rep}}$  where  $D_{\text{rep}}$  is the repulsive diameter of the pair interaction, cf. the discussion in Refs. 15, 17) and  $k = k_F$  (resulting from the Peierls distortion of the packing by the medium and long-range oscillation in the pair potential with the Friedel wavelength  $\lambda_F = 2\pi/2k_F$ ). The important point is that with increasing frequency, the 'structural' peak is more strongly damped than the 'electronically induced' peak in  $S(k, \omega)$ .

In the longitudinal current correlation function  $C_l(k, \omega)$  (Figs. 5(a, b)) we find at low energies a sharp sound-wave peak and a structural peak split by electronic effects. At



**Figure 4** Dynamical structure factors  $S(k, \omega)$  at low energies for liquid Ge (a) and As (b) (see text).





**Figure 5** Longitudinal current correlation function  $C_l(k, \omega) = (\omega^2/k^2)S(k, \omega)$  for liquid Ge (a) and As (b).

higher energies the two sub-peaks merge into a broad inelastic peak that shifts to smaller wavenumbers and meets the sound-wave peak at the highest frequencies.

#### IV DISCUSSION AND CONCLUSIONS

Our results demonstrate that in polyvalent liquid elements an unexpected electronically induced softening of the eigenfrequencies of propagating collective modes exists

at wavevectors corresponding to the diameter of the Fermi-sphere. In accordance with our interpretation of the liquid structures of these elements<sup>14,15,17</sup> as arising from a Peierls-like modulation of the atomic packing by the Friedel-oscillations in the interatomic pair-potential, the mode-softening may be attributed to a Kohn-anomaly<sup>30</sup> in the vibrational spectrum. In a material with delocalized electrons, a Kohn anomaly can be considered as a resonance between the collective excitation (the 'phonon') and the electrons at the Fermi-surface responsible for the long-range oscillations in the screening. It is also an interference effect of the long-range Friedel-oscillations in the interatomic forces. If the electrons have a finite mean free path  $l$  due to disorder-scattering, this will lead to an exponential damping of the long-range oscillations by a factor  $\exp(-r/l)$  and correspondingly broaden the Kohn anomaly over a width  $\delta k \sim 2\pi/l$ , but it will not suppress the Kohn anomaly.

The Kohn anomaly in the spectrum of collective excitations in polyvalent liquid metals should be observable in inelastic neutron scattering. In fact, the differences in the dynamical structure factors of l-Pb and l-Bi observed by Larsson, Dahlborg and co-workers have to be attributed to this effect. In l-Bi the anomaly is rather weak because the 'on-Fermi-surface' matrix-elements of the pseudopotential is small (in l-Pb it is completely suppressed since the matrix-element is nearly zero)<sup>17</sup>. The stronger pseudopotential in l-Ge and l-As leads to stronger structural and dynamical effects. We hope that our study will stimulate such experiments. The present investigation has certainly a preliminary character because of the limited validity of the viscoelastic approximations. We are now preparing an extensive molecular dynamics study, combined with a mode-coupling analysis, of the dynamical properties of these elements.

#### Acknowledgements

This work has been supported by the Austrian Ministry of Research within the East-West Cooperation Program under project. no GZ 45.007/24-27/91. G. K. acknowledges the support from the Fonds zur Förderung der wissenschaftlichen Forschung (Proj. No. P8912) and the Oesterreichische Nationalbank (Proj. No. 4649).

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