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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 Meyer, A. , Silbert, M. and Young, W. H.(1984) 'The Signature of Long Range Interatomic Forces in Observed Liquid Structure Factors', *Physics and Chemistry of Liquids*, 14: 1, 1 – 11

To link to this Article: DOI: 10.1080/00319108408080791

URL: <http://dx.doi.org/10.1080/00319108408080791>

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The Signature of Long Range Interatomic Forces in Observed Liquid Structure Factors

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(Received October 24, 1983)

Observed liquid structure factors are now known to provide, through their behaviour beyond their principal peaks, useful but limited information about interatomic core forces. It is argued that they also carry, below their principal peaks, the signatures of the interatomic tail characters. This proposition is illustrated by tests on cases of different type where the forces are either known or can be plausibly conjectured. In particular, the difference between metals and insulators can be distinguished.

1 INTRODUCTION

The ability to extract useful information from observed liquid structure factors was first demonstrated by March and coworkers.^{1,2} In fact these writers derived interatomic potentials which, in favourable cases, showed the qualitative differences expected between insulators and metals. After that time, however, doubt was cast on the accuracy of the then favoured liquid state approximations (Born–Green, Percus–Yevick, hypernetted chain) as well as the accuracy of some of the then available experimental data. The confused situation thus resulting is perhaps best summed up on page 19 of Waseda's textbook.³

In the meantime there have been developments in theory and experiment³ and the question once again arises: What information about the interatomic forces can be extracted from a good observed structure factor? In the work

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below we use some recent developments in the theory, as well as up-to-date measured data, to suggest that information is thus forthcoming on inter-atomic force tails and that, in particular, metals and insulators are in this way distinguishable.

An important development of the theory was due to Weeks *et al.*⁴ who showed that for Lennard-Jones liquids, the cores decided the structure factor beyond the first peak. Their quantitative treatment of the core-only problem (the WCA theory) was reformulated by Jacobs and Andersen⁵ and in this form it was found that one could start from cores which were not too soft and obtain agreement between theory and (computer) experiment, in favourable cases, around the second and third peaks.

The present writers⁶ emphasized the non-uniqueness of the core forces leading to an observed structure factor using the WCA formalism. By a simple accurate approximation, they showed that, essentially, only an effective diameter and a corresponding force are needed to describe the high argument behaviour. In a later publication,⁷ it was shown how, conversely, a diameter and force could be extracted from observed data.

Very recently, the above conclusion was well illustrated by Hayter *et al.*⁸ ‡ These authors, using the mean spherical approximation, took the entirely repulsive short-range potential obtained by the Thomas–Fermi screening of an empty core pseudopotential and, by suitable adjustment of the parameters, were able to obtain excellent agreement with experiment down to very low arguments. Indeed the agreement is so good that it might plausibly be postulated that no tail effects can be extracted from observed data.

The object of the work below, however, is to show that at least qualitative information on tail forces lies in the low argument region of observed structure factors and, in particular, we confirm March *et al.*'s conclusion that metals and insulators can, in principle, be distinguished in this way.

Below, in Section 2, we demonstrate the effect of the cores on the structure factors and then, in Section 3, indicate how the residual features, after core effects have been subtracted, provide some account of the tails. The situation is summarized in Section 4.

2 ATOMIC CORES

The procedure we follow is best explained by introducing the direct correlation function, $c(q)$, which is related to the structure factor $S(q)$ through the Ornstein–Zernike relationship

$$nc(k) = 1 - S^{-1}(k) \quad (1)$$

Here n is the number density of the atoms.

‡ For another interesting approach to the same problem, see Matthal.⁹

A fluid with only short-range strongly repulsive pair potentials (which we will call core potentials) is described in zeroth order by hard spheres. Weeks *et al.*⁴ showed, however, that a suitably defined "blip" function $B(k)$ could account for the core shape. In the reformulation of this theory due to Jacobs and Andersen⁵ one writes

$$C_{\text{core}}(k) = C_{\text{hs}}(k) + B(k) \quad (2)$$

where $C_{\text{hs}}(k)$ is the direct correlation function for hard spheres of diameter σ , say.

The direct correlation function for hard spheres is known with high accuracy¹⁰ and it is not necessary for present purposes to specify the detailed general form of $B(k)$. It is enough to say that in the approximation used by the present authors^{6,7} $B(k)$ contains only the parameters σ , $u_{\text{core}}(\sigma)$ and $u'_{\text{core}}(\sigma)$ to reflect the full potential $u_{\text{core}}(r)$. It thus becomes a fairly straightforward matter to use Eqs (1) and (2) to calculate a structure factor from a postulated potential.

Conversely, if we believe that an observed structure factor arises entirely from a core potential, by fitting we can determine the relevant σ , $u_{\text{core}}(\sigma)$ and $u'_{\text{core}}(\sigma)$. In fact, the experience of Jacob and Andersen suggests that we might reasonably believe this to be true for large q (from around the second and third peaks). When a poor fit is obtained, this is most likely due not to the failure of the general hypothesis but to the loss of accuracy of the particular description furnished by Eq. (2) when a softish potential is involved.

In Figure 1 we show examples of the large q fits of theory to experimental data for liquids of inert gases,^{11,12} repulsive inverse power potentials¹³ (obtained by computer) and noble metals.³ Overall, we regard these as tolerably satisfactory in the light of the remarks of the previous paragraph. The associated numerical data for these and other similar cases are given in Table I.

TABLE I
Analysis of observed structure factors; data summary

Input			Output				
System	T/K	$n/\text{\AA}^{-3}$	A	η	$\sigma/\text{\AA}$	$u_{\text{core}}(\sigma)/\text{eV}$	$-\sigma u'_{\text{core}}(\sigma)/\text{eV}$
Ar	85	0.0213	0.0529	0.492	3.535	0.00675	0.1312
Ne	35	0.0317	0.0468	0.402	2.894	0.00248	0.0387
	35	0.0334	0.0564	0.426	2.900	0.00260	0.0396
	35	0.0347	0.0689	0.445	2.904	0.00272	0.0395
r^{-12}	68.6	0.0253	0.0803	0.519	3.396	0.00599	0.1025
r^{-9}	50.6	0.0253	0.0904	0.515	3.386	0.00446	0.0710
r^{-6}	25.3	0.0253	0.0975	0.517	3.390	0.00226	0.0348
r^{-4}	12.2	0.0253	0.1010	0.512	3.381	0.00109	0.0163
Cu	1423	0.0755	0.0797	0.526	2.369	0.1247	2.196
Ag	1273	0.0518	0.0944	0.514	2.667	0.1133	1.750
Au	1423	0.0526	0.0830	0.510	2.646	0.1233	2.012

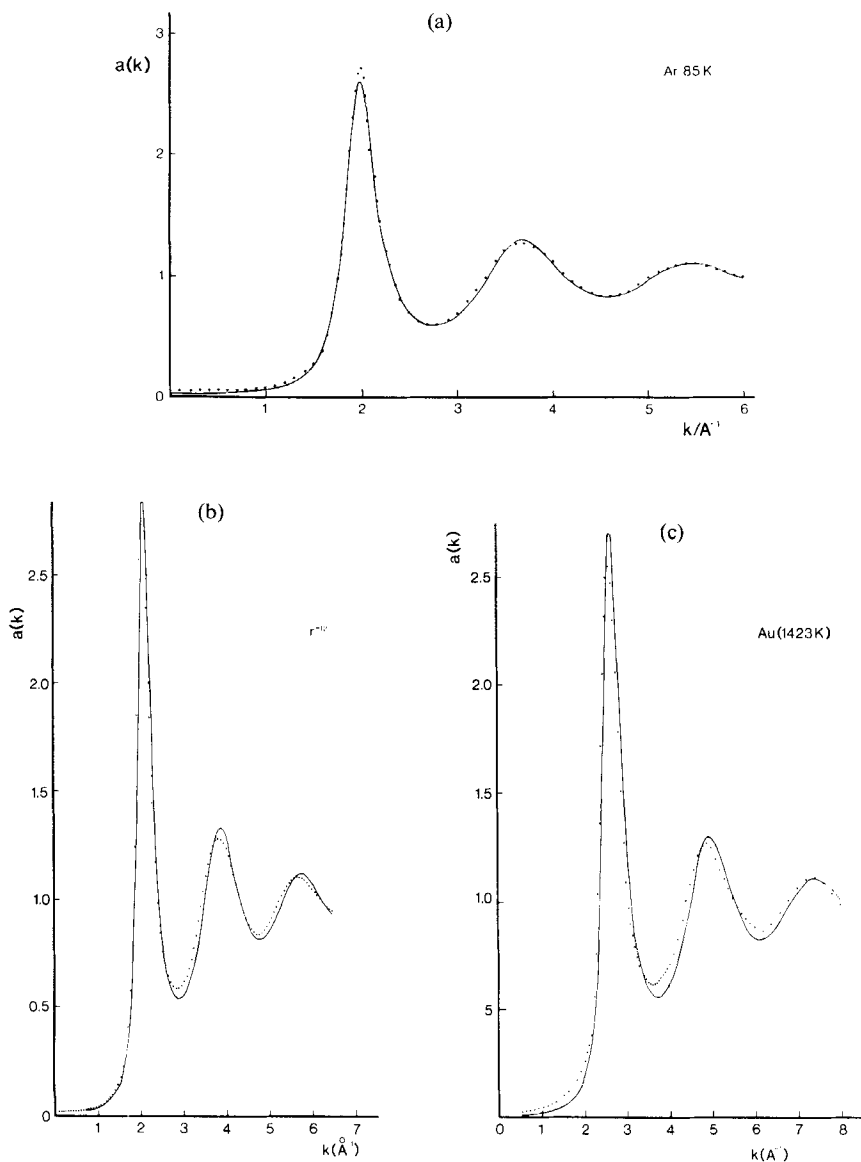


FIGURE 1 Large k fit of theory (lines) to experiment (dots) for three types of liquid: (a) argon; (b) r^{-12} ; (c) gold. The fitted parameters are included in Table I.

3 ATOMIC TAILS

Now suppose that a fluid is characterized by an interatomic potential expressible as the sum of core and tail parts. The core-only problem can be solved as in Section 2 and we will use the terminology u_{core} , c_{core} , etc. introduced there in the present context.

To include the effect of the tail part of the potential, we can use the random phase approximation to write

$$c(k) = c_{\text{core}}(k) - u_{\text{tail}}(k)/k_B T \quad (3)$$

This approximation provides predominantly low k corrections and, although not the full story, experience suggests¹⁴ it is always qualitatively and often quantitatively accurate.

From Eqs (1) and (3) we now have

$$u_{\text{tail}}(k) = S^{-1}(k) - S_{\text{core}}^{-1}(k) \quad (4)$$

If $S(k)$ is given (experimentally) and $S_{\text{core}}(k)$ is available (by the method of Section 2), then Eq. (4) can be Fourier inverted to give the tail in real space. (In this respect the method follows closely one proposed recently by McLaughlin and Young¹⁵ and the present paper may be viewed as an extension of that work.) The results obtained for the systems core-analysed in the previous section are shown in Figures 2–4.† The known result (in the repulsive inverse power cases) or the physically anticipated behaviour (for the inert gas and liquid metals) is in each case qualitatively reproduced.

It is of interest to see how these distinctive characteristics arise, so we examine them in Fourier transform by plotting, in Figure 5, the right side of Eq. (4) (slightly smoothed) in typical cases. The curve for Ar is described well by a Gaussian. Since quite a Gaussian transforms as a Gaussian, this explains the qualitative (negative definite) shape of the tail shown in Figure 2(a).

The shapes shown in Figure 5 for the inverse power potentials have negative minima at $k = k_0$ ($\approx 1 \text{ \AA}^{-1}$ for r^{-12} , $\approx 1.5 \text{ \AA}^{-1}$ for r^{-6}). This ensures that the corresponding tails in Figure 3 are positive at $r \approx 3\pi/2k_0$ and decay thereafter. This is roughly the behaviour of the curves found by detailed calculation.

The curve shown for Au in Figure 5 has the character of a smoothed negative step function with edge at $k_0 \approx 1.4 \text{ \AA}^{-1}$. On transforming such a

† We do not have enough information to match uniquely core to tail. For visual effect, we have drawn a linear core potential of the slope indicated in Table I and such that its intersection at $r = r_{\text{int}}$ with the tail satisfies $u(\sigma) - u(r_{\text{int}}) = u_{\text{core}}(\sigma)$ of Table I. This is in the spirit of the WCA division.

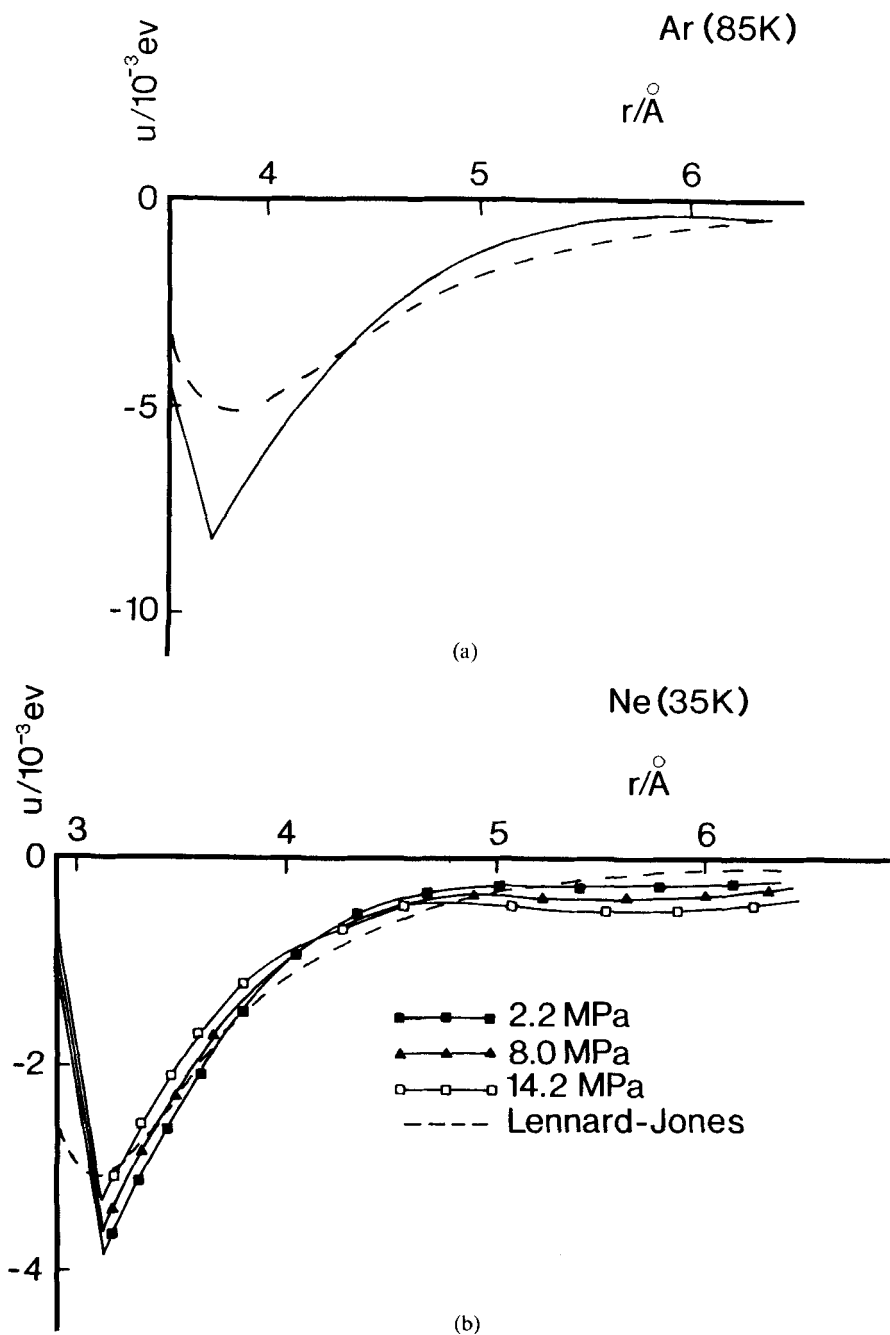


FIGURE 2 Interatomic potentials deduced from observed structure factors of the inert gas liquids: (a) argon; (b) neon at three different pressures. The Lennard-Jones potentials (broken curves) correspond (in a conventional notation) to $\epsilon/k_B = 116.4$ K and $\sigma(\text{LJ}) = 3.37$ Å for argon¹⁶ and $\epsilon/k_B = 35.5$ K and $\sigma(\text{LJ}) = 2.75$ Å for neon.¹⁷ These parameters are obtained by fitting to independent data (the gas virial coefficients). Note that the neon curves are insensitive to pressure, as one might expect.

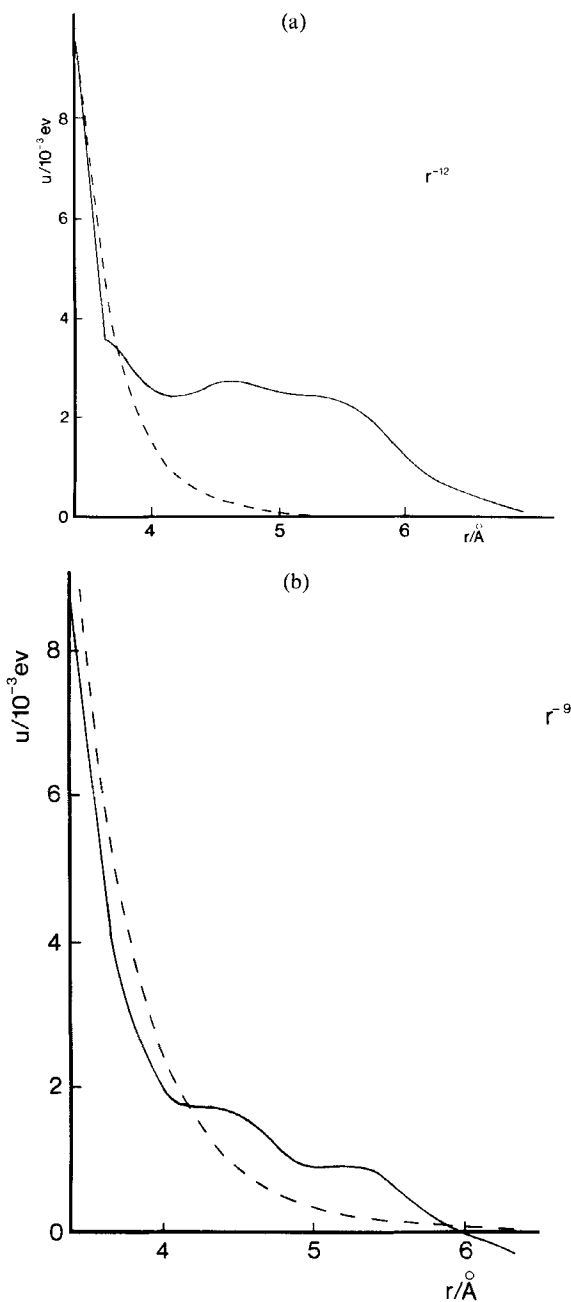
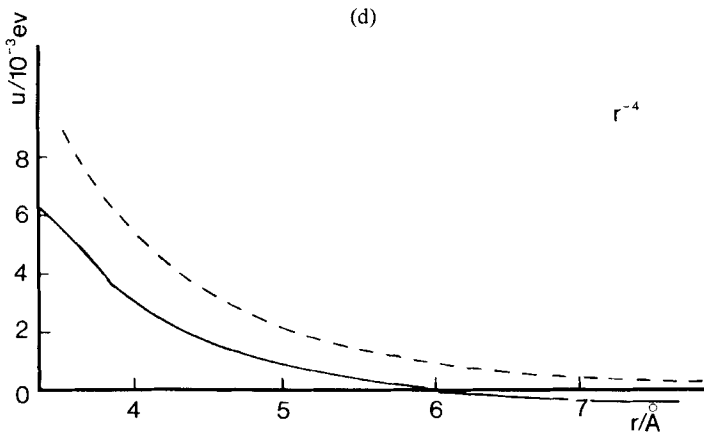
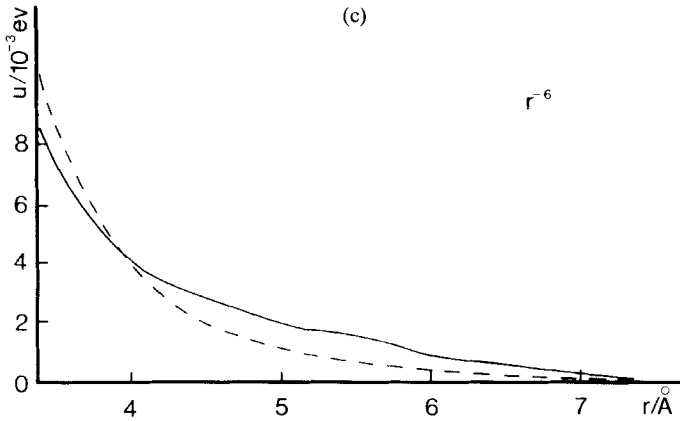


FIGURE 3 Interatomic potentials deduced from structure factors computer calculated from repulsive inverse power potentials of type: (a) r^{-12} ; (b) r^{-9} ; (c) r^{-6} ; (d) r^{-4} . It is possible, in these cases, to record also the known results (broken curves) for comparison purposes.



FIGURES 3c, d

function, we expect decaying oscillating behaviour with a positive portion between $4.5/k_0$ and $7.7/k_0$ much as seen in Figure 4.

It should be remarked that the noble metals were studied in this work because one might reasonably expect to obtain tails of alternating sign, this being the result predicted by second order pseudopotential perturbation theory.^{18,19} However, the effective pairwise interaction responsible for the observed structure factor is known,^{20,21} in the case of polyvalent simple metals, to contain higher order (many body) terms which camouflage the

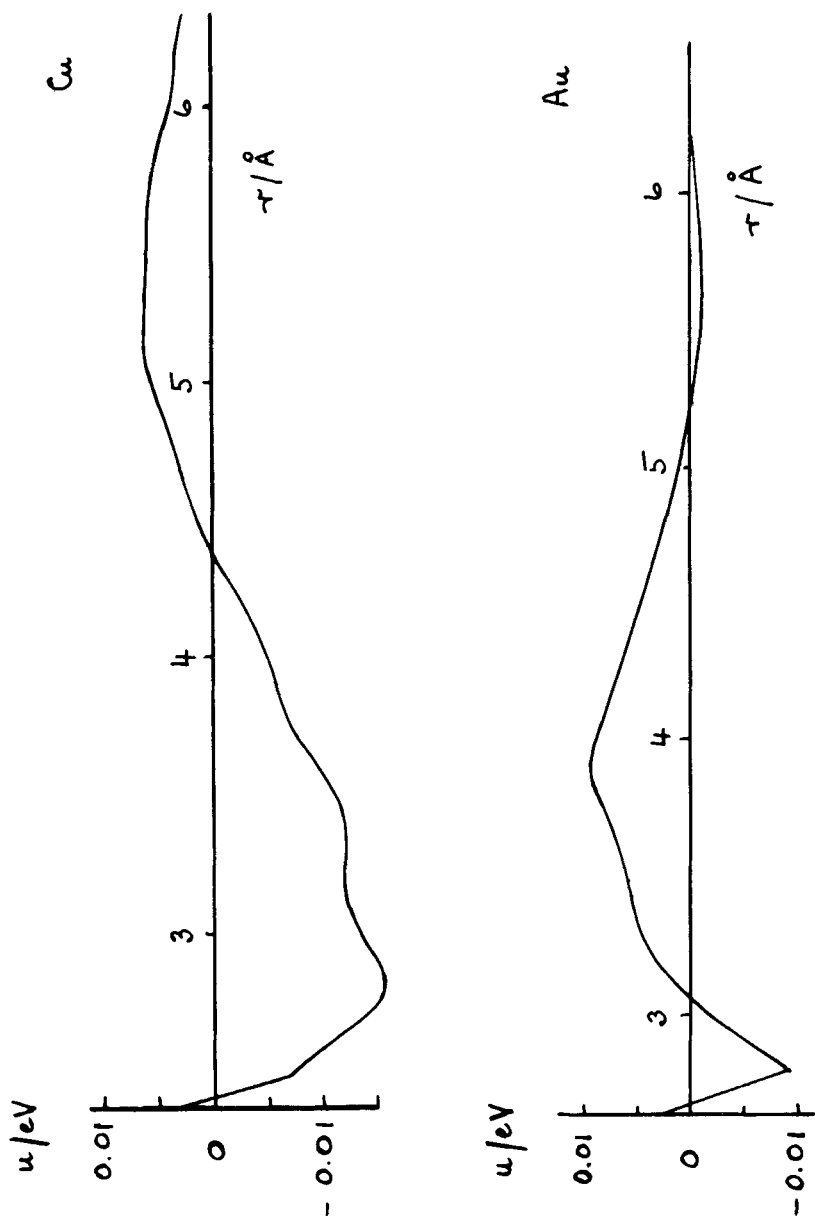


FIGURE 4 Interatomic potentials deduced from observed structure factors of noble metals. Oscillatory behaviour, expected on physical grounds,^{18, 19} is evident.

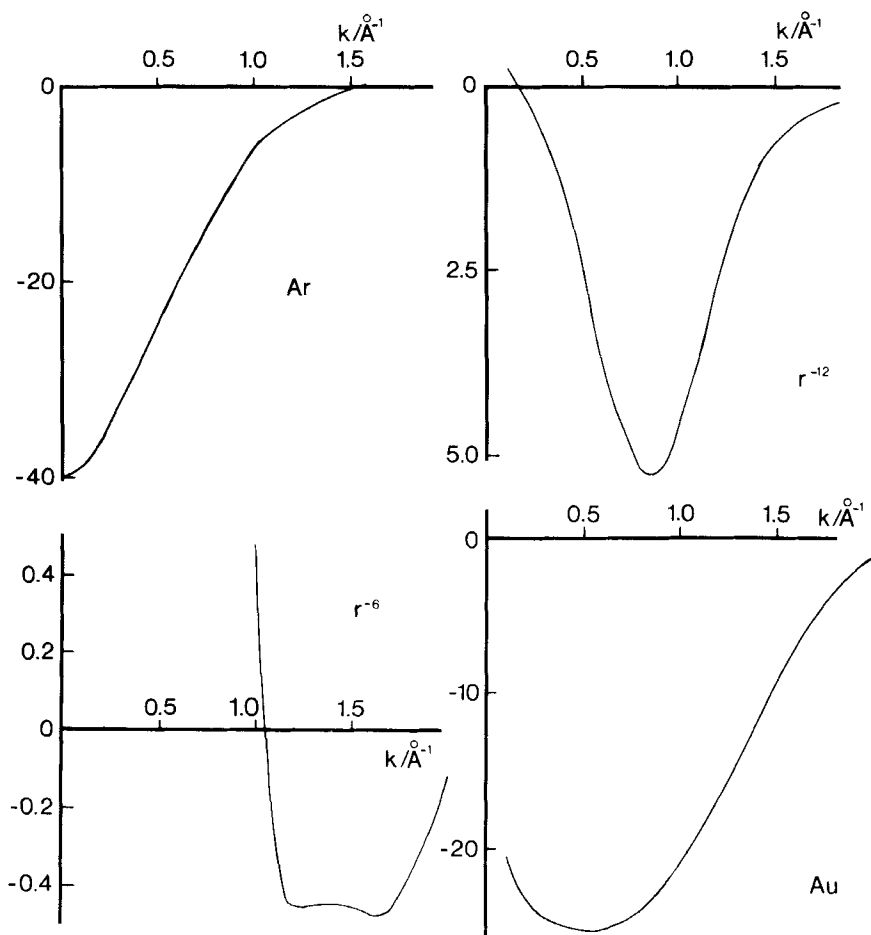


FIGURE 5 $S^{-1}(k) - S_{\text{core}}^{-1}(k)$ versus k for four cases. S is observed and S_{core} is obtained by fitting the core theory to S at large k .

lowest order result. The monovalents are the obvious candidates for good convergence of the perturbation series. With the alkalis excluded because of their soft cores, one was left to see if the noble metals would suffice. Apparently, they do.

4 CONCLUSIONS

It would appear that the high k character (beyond the first peak) is dominated by the core size and shape (the latter in effect being specified by a single parameter). When this feature is removed from the structure factor (or, more

precisely, the direct correlation function) the residual data carry sufficient information to infer features of the atomic tail of the effective pairwise interaction.

Acknowledgement

We are grateful for the support of the U.K. Science and Engineering Research Council.

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