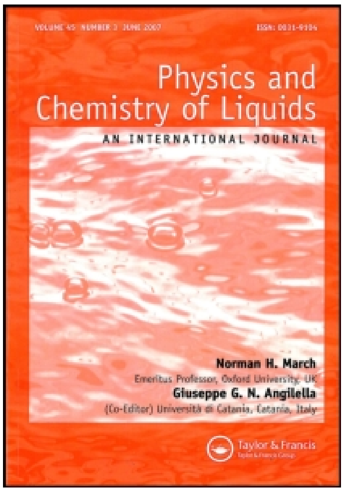

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Effective Interatomic Pair Potentials in Liquids via the WCA and RPA Methods

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Letter

Effective Interatomic Pair Potentials in Liquids via the WCA and RPA Methods

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A method which combines features of the WCA and RPA approximations is proposed for calculating an effective interatomic pair potential from an observed structure factor. The method is tested on Ne and gives a plausible result; it is then applied to Al, In and Pb and for this sequence there is evidence of the increasing importance of many-ion and density-dependent forces.

Since the initial work of March and coworkers[1,2] there has been much interest in the problem of determining the effective interatomic pairwise potential $v_{\text{eff}}(r)$ corresponding to a given liquid-state structure factor $a(q)$. Many methods of approximate solution have been devised but it is probably fair to say that no one method has emerged as best, even for monatomic uncharged fluids.

In the course of work at present in progress (see, also, McLaughlin, Silbert and Young[3]) we have arrived at yet another method. It appears to be competitive in accuracy with those used hitherto and seems to us to be worth recording. The low argument values of $a(q)$ must be available (here and in other procedures) before a meaningful calculation can be attempted. This severely limits the range of applications at the present time. Nevertheless, enough information is available for Ne and a few liquid metals and some results based on these data are reported below.

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The method is as follows:

i) Take a positive definite repulsive potential $v_{\text{core}}(r)$ to represent the core. This should be parametrized and the parameters adjusted so that a WCA calculation, in the modification proposed by Jacobs and Andersen,[4] yields a structure factor $a_{\text{core}}(q)$ such that $a_{\text{core}}(q) \approx a(q)$ at large q.

ii) Then calculate the tail potential from the RPA formula

$$v_{\text{tail}}(r) = \frac{k_B T}{(2\pi)^3 n} \int_0^\infty \left\{ \frac{1}{a(q)} - \frac{1}{a_{\text{core}}(q)} \right\} \frac{\sin qr}{qr} 4\pi q^2 \, dq, \tag{1}$$

n being the ionic number density. The total effective potential is then

$$v_{\text{eff}}(r) = v_{\text{core}}(r) + v_{\text{tail}}(r). \tag{2}$$

The rationale for the above procedure may be stated thus:

i) We assume the validity of the WCA splitting (Eq. (2)) of the effective potential into a core part and a relatively weak tail, the former being responsible for the structure factor at large q and the latter for modifications at small q. An a posteriori test is that inside the core

$$|v'_{\text{tail}}(r)| \ll |v'_{\text{core}}(r)|. \tag{3}$$

ii) Jacobs and Andersen modified the original WCA method by introducing a structure factor formula for $a_{\text{core}}(q)$ which is correct at larger q (well beyond the principal peak). More recently, the same modification has been shown by Telo da Gama and Evans[5] to have a low q validity also. Therefore, it seems realistic to use the result $a_{\text{core}}(q)$ as a base from which to assess the effect of $v_{\text{tail}}(r)$.

iii) The RPA method of evaluating the correction to $a_{\text{core}}(q)$ from $v_{\text{tail}}(r)$ is not the whole story as it does not fully incorporate the effect of long wavelength density fluctuations. This can have quantitative implications[3] but, in our experience (work in progress), it does not qualitatively alter the RPA result. Equation (1) should therefore give useful information if cautiously used.

We next turn to a few practical details relating to our characterisation of the cores.

i) According to Meyer, Silbert and Young,[5] the large q part of the structure factor reflects little of the detail of $v_{\text{core}}(r)$ beyond an effective diameter σ and a slope $v'_{\text{core}}(\sigma)$ so that an assumed linear form of $v_{\text{core}}(r)$ is probably as good as anything more complicated. However, convenience can also dictate the choice of parameterized form (as below).

ii) The ancillary hard sphere system through which $a_{\text{core}}(q)$ is defined is taken to be as described by Verlet and Weis;[7] because of the quality of agreement between the predictions of this and machine calculations, it is believed to be highly accurate.

iii) The parameters used by us were adjusted so as to satisfy the criterion

$$\int_{q_1}^{q_5} \{a(q) - a_{\text{core}}(q)\}^2 q^2 \, dq = \text{minimum} \tag{4}$$

where q_1 and q_5 are the first and fifth nodes of $a(q) - 1$ after the principal peak. This is a somewhat arbitrary procedure but seems a fair recognition that the true $a_{\text{core}}(q)$ merges with $a(q)$ asymptotically but that the accuracy of observations often diminishes at large q.

iv) In the case of Ne we chose a truncated Lennard–Jones potential $\varepsilon\{2r_0/r)^6 - 1\}^2$ and adjusted the two parameters ε and r_0. For the metals we used the core part of the interatomic potential obtained by Ashcroft pseudopotentials and Vashishta–Singwi screening theory. This was purely for reasons of convenience since we already had this programme set up.[3] Our best fit parameters are quite close to conventional choices (Table 1).

TABLE I

Best fit parametrizations according to Eq. (3) compared with conventional values

Liquid	Parameter	Best fit	Conventional	
Ne	ε/k_B	30.6	35.5	Refs 8,13
	r_0/a_0	5.39	5.20	
Al	r_c/a_0	1.12	1.12	Ref. 14
In	r_c/a_0	1.34	1.32	
Pb	r_c/a_0	1.51	1.47	

Note that the present best-fit parameters only describe the core (by the method explained in the text) whereas the conventional parameters purport to describe the whole potential.

The large q fit to the observed data of de Graaf and Mozer[4] for Ne is shown in Figure 1, the corresponding potential, v_{core}, being as in Figure 2(a). The information in Figure 1 then went into Eq. (1) and v_{tail} of Figure 2(a) was obtained. The two parts, v_{core} and v_{tail} are added to obtain the curve v_{eff}. At $r = \sigma$ (the WCA diameter), $|v'_{\text{core}}| \approx 4|v'_{\text{tail}}|$ so that Eq. (3) is moderately well satisfied. Our result for v_{eff} is quite close to the result one might anticipate from other evidence. For example, the full Lennard–Jones form

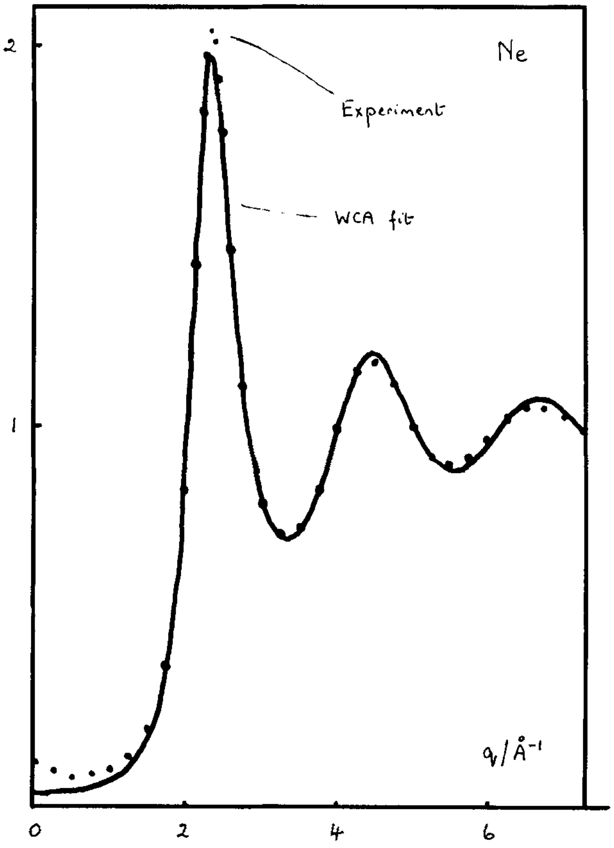


FIGURE 1 Structure factor of Ne at 35.05 K and 79.0 atm. The continuous line is the best-fit WCA result using a truncated Lennard-Jones core (the parameters being as in Table I). The points are observed (de Graaf and Mozer (1971).

with the *conventional* parameters of Table I inserted is shown in Figure 2(a). It compares rather well with v_{eff} and much better than the corresponding curves obtained by the Percus–Yevick and hypernetted chain methods (as Figure 5 of de Graaf and Mozer indicates). We regard this result for Ne as a demonstration of the usefulness of the present method.

We next turn to the metals Al, In and Pb. Here much less is known about the potentials and these become the focus of our subsequent investigation. We use the data of Waseda[9] to obtain the curves shown in Figures 2(b)–(d). It will be seen that criterion (3) is well-satisfied for In and Pb, though less so for Al. (We ignore any worries on the latter score since we do not know how to mend matters at this level of sophistication). Electron theory predicts

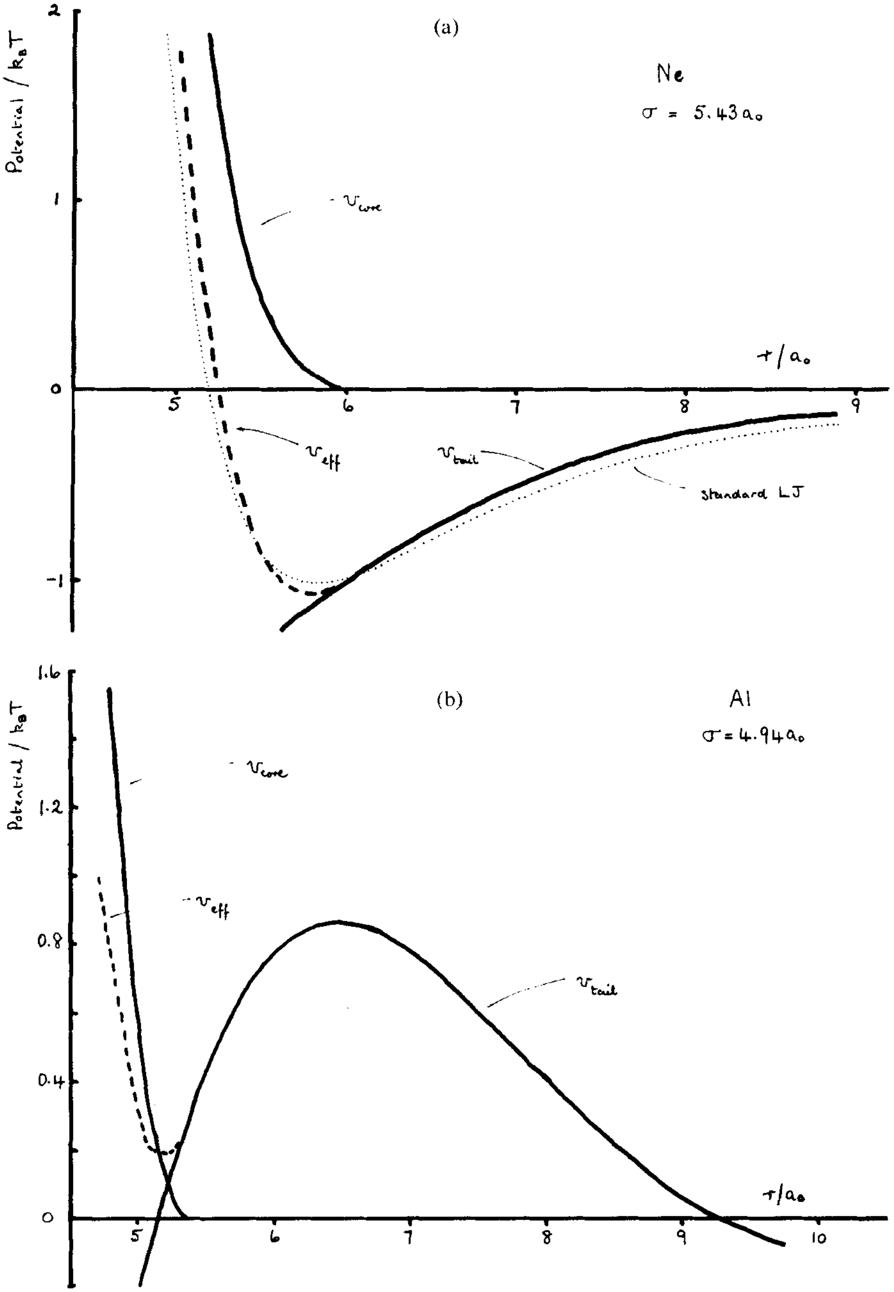
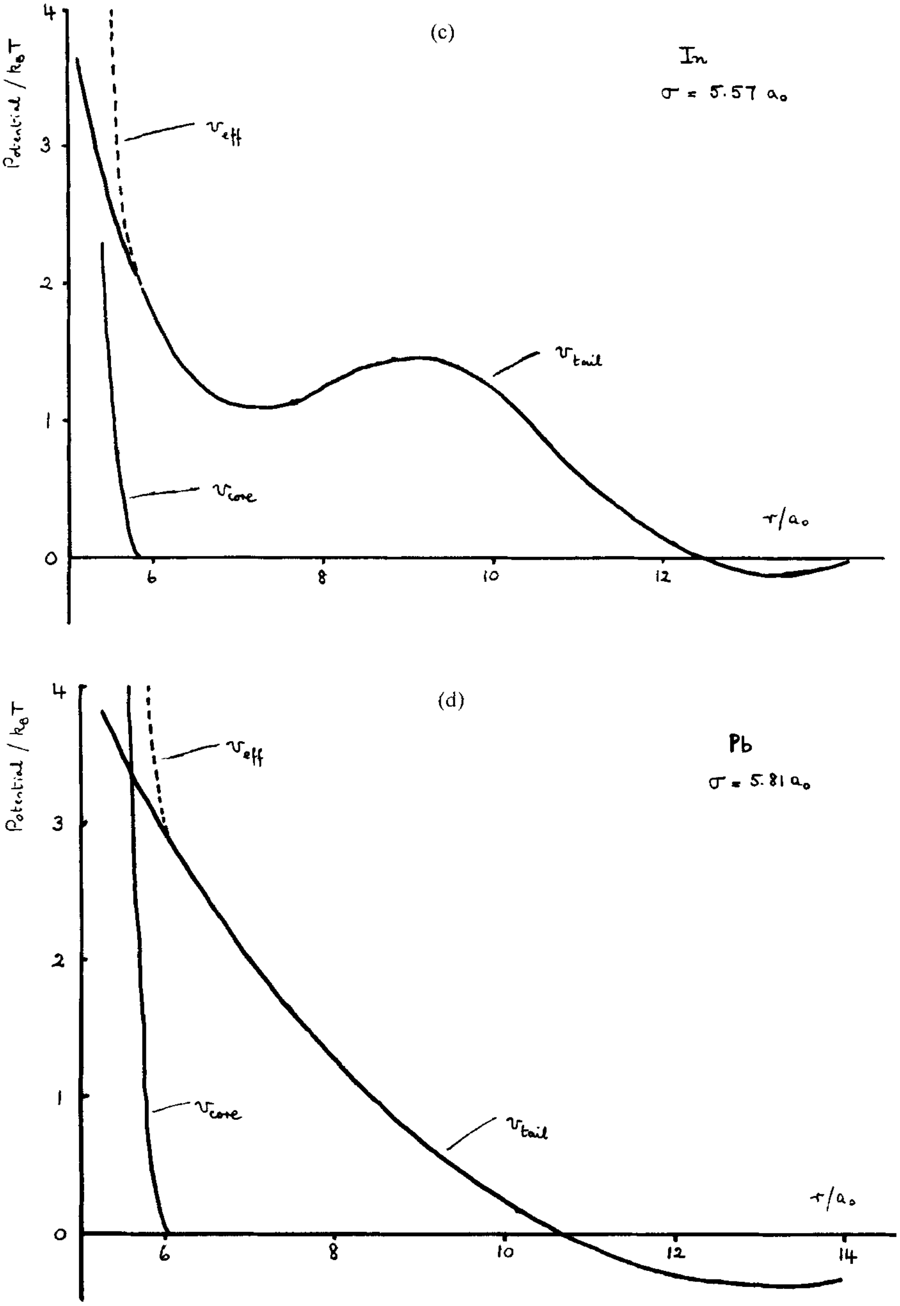


FIGURE 2 Effective potential and its core and tail parts (cf. Eq. (2)): (a) Ne at 35.05 K and 79.0 atm., (b) Al at 943 K and 1 atm., (c) In at 433 K and 1 atm., (d) Pb at 613 K and 1 atm. In the case of Ne we have also included (dotted) a Lennard–Jones core (the parameters being as in Table I). The points are observed (de Graaf and Mozer 1971).


(c)
In
σ = 5.57 a₀
Potential / k_B T
4
3
2
1
0
v_eff
v_tail
v_core
r/a₀
6
8
10
12
(d)
Pb
σ = 5.81 a₀
Potential / k_B T
4
3
2
1
0
v_eff
v_core
v_tail
r/a₀
6
8
10
12
14

FIGURES c,d

an oscillatory interaction and something of this sort is found. It also predicts, just beyond the core, a deep negative-value minimum only vestiges of which are obtained for Al and In and of which none remains for Pb.

Hasegawa and Young[10] suggested that such shapes might occur even in pair potentials deduced without approximation and would be a manifestation of many-body and/or density-dependent forces (see, also, Faber).[11] From our discussion earlier above of Eq. (1), it is evident that, within the present approximations, the effect could also arise, at least in part, from the incomplete treatment of the density fluctuations by the RPA.

For Al, the many-body and/or density-dependent forces aspect may not be large[12] and the density fluctuation effect might be important.[3] Thus it is to the forcible subsuming of the latter effect into the RPA that we are inclined to ascribe the raised principal minimum in $v_{\mathrm{eff}}(r)$ in this case. For In and (especially) Pb, however, it is difficult to resist the conclusion that many-body and/or density-dependent forces play some significant role. This conclusion for Pb is in agreement with that of Hasegawa and Young[12] reached by a different route.

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