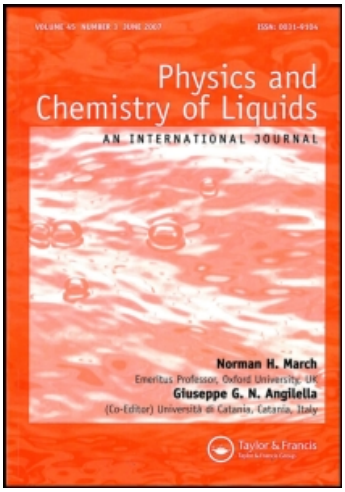

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Soft Sphere Characterisation from Liquid Structure Factors; Application to Lead

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Letter

Soft Sphere Characterisation from Liquid Structure Factors; Application to Lead

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We adapt the WCA theory so as to provide a convenient formalism for gauging core softness from the evidence of a measured liquid structure factor. The method is illustrated for lead.

This letter concerns the interpretation of liquid structure factors $a(k)$ at large k (roughly, beyond the principal peak), attention thus being focussed on the cores of the interatomic potentials. A useful picture for many purposes[1] is to regard the ions of a liquid, at fixed temperature and density, as hard spheres of diameter σ. Unfortunately, the corresponding structure factor $a_\sigma(k)$, which is known to high accuracy,[2] is never flexible enough to match observation. A next logical step is to examine the effects produced by one further parameter and we do this by introducing a finite force at the effective diameter distance. The details are as follows.

We begin with the Jacobs and Anderson[3] (JA) version of the WCA theory in which

$$a^{-1}(k) = a_\sigma^{-1}(k) - n\tilde{B}(k) \tag{1}$$

Here, n is the number density and $\tilde{B}(k)$ the Fourier transform of the usual WCA blip function. On imposing the WCA condition

$$\tilde{B}(0) = 0 \tag{2}$$

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there is a straightforward procedure for evaluating $a(k)$ from (1) for any postulated repulsive potential, $u(r)$. Such a result can then be usefully compared with experiment at higher k (JA, loc. cit.).

Recently, Meyer, Silbert and Young[4] (hereafter I) emphasised the non-uniqueness, on the basis of available data at least, of the potentials thus obtained, and have shown that, for given fairly hard cores, $a(k)$ reflects little more than an effective diameter σ and an effective force $-u'(\sigma)$ at $r = \sigma$. Below, we show that conversely the formalism of I provides a working tool for extracting such information with fair precision from experimental data.

A first relationship (I, Eq. (11)) arises from the implementation of Eq. (2) and is

$$U = \frac{-\beta\sigma u'(\sigma) + Y + 2}{-2\beta\sigma u'(\sigma) + Y + 2} \tag{3}$$

where $U = \exp\{-\beta u(\sigma)\}$ and $Y = \{\partial \ln g_\sigma(r)/\partial \ln r\}_{r=\sigma+0}$. The Verlet–Weis radial distribution function $g_\sigma(r)$ for hard spheres as well as Y are given in the Appendix to I.

A second result (I, Eq. (6), first non-vanishing term only) is an expression for $\tilde{B}(k)$. When this is simplified using (3), and substituted into (1), we obtain

$$a^{-1}(k) = a_\sigma^{-1}(k) + A\{\cos k\sigma - (\sin k\sigma/k\sigma)\} \tag{4}$$

where

$$A = \frac{16\eta g_\sigma(\sigma + 0)}{(Y + 2)^2} \frac{(U - \frac{1}{2})^2}{U(1 - U)} \equiv \mu \frac{(U - \frac{1}{2})^2}{U(1 - U)}. \tag{5}$$

In practice we fit (4) to the observed data beyond the principal peak. When the optimum σ and A are found, Eq. (5) solves to give

$$U = \tfrac{1}{2}\left\{1 - \left[1 + \frac{\mu}{A}\right]^{-1/2}\right\} \tag{6}$$

and (3) then yields

$$-\beta\sigma u'(\sigma) = -\tfrac{1}{2}(Y + 2)\left\{\left[1 + \frac{\mu}{A}\right]^{1/2} + 1\right\} \tag{7}$$

Let us apply this procedure to the data of Waseda[5] for lead at 340°C. Our precise fitting procedure was to minimize

$$\int_{k_1}^{k_2} \{a_{\text{expt}} - a\}^2 k^2 \, dk$$

where $a(k)$ is given by (4) and k_1, k_2 correspond to the first and fifth nodes of $a(k) - 1$ beyond the principal peak. The result shown in Figure 1 implies

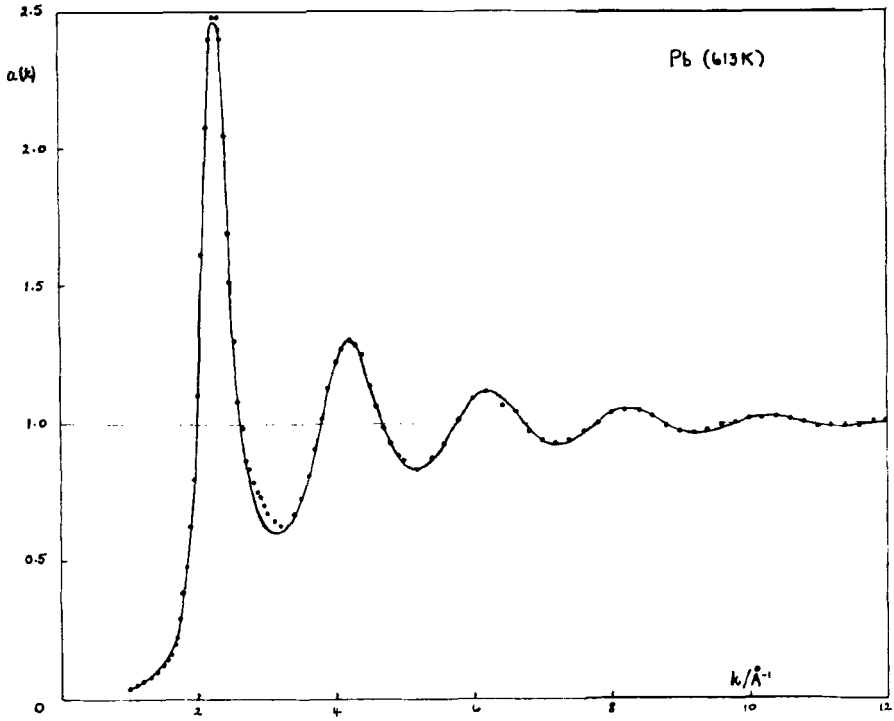

FIGURE 1 Structure factor for lead at 613 K. Points: experiment (Waseda[5]); continuous line: theory (Eq. (4) and parameters of Table I).

that any reasonable criterion would have yielded much the same fit. (We exclude from this analysis the small anomaly near $k = 3$ Å for which there exist a plethora of explanations.[6–9])

Waseda provides structure factors for lead at three higher temperatures and a similar quality of fit is achieved there also. The results thus obtained may be collated as follows. First, we show in Table I the output for σ and A.

TABLE I

Structure factor analysis for lead

Input		Output			
T/K	$n/\text{Å}^3$	σ/Å	A	$u(\sigma)/mRy$	$-\sigma u'(\sigma)/mRy$
613	0.03099	3.096	0.039	3.41	75
823	0.03022	3.060	0.046	4.53	84
1023	0.02950	3.011	0.040	5.36	97
1173	0.02870	2.991	0.046	6.12	96

There is the expected decrease in σ as T increases, the packing fraction decreasing from 0.48 to 0.40 over the temperature range studied. On the other hand, we find no clear trend for A, a rather constant value in the range 0.040–0.045 Å being indicated. Next we examine the potential parameters, and these establish the qualitatively reasonable picture of a potential which rises increasingly fast as the interatomic distance is diminished.

There is a useful test of internal consistency contained within Table I. The four $u(\sigma)$ manifest quite good average linear behaviour versus σ, the slope being 24 mRy Å^{-1}. This is precisely the result one obtains from columns 3 and 6 for 613 K, the higher temperature results being a little larger. In making this point, one notes that while in principle one is sampling, at each temperature, a different curve, in practice this complication is probably ignorable because of the limited density variation involved.

In summary, we have shown that the measured structure factors for lead (excluding the low angle region and 3 Å anomaly) contain only limited information on the interatomic potential. That, however, which is present can be cross-checked and consists of credible core size and softness parameters.

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