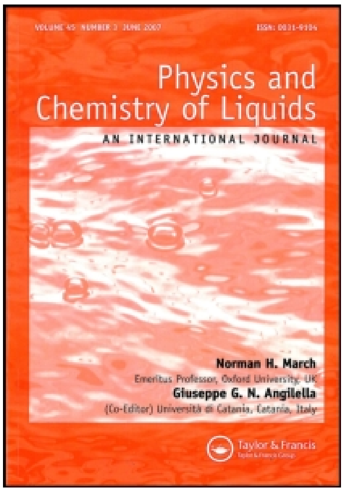

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Structure Inversion: Pair Potentials with Common Characteristics from Three Theories at Low Density on Liquid—Vapour Coexistence Curve of Cs

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LETTER

Structure Inversion: Pair Potentials with Common Characteristics from Three Theories at Low Density on Liquid–Vapour Coexistence Curve of Cs

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Pair potentials with common features are shown to follow from three approximate theories for a low density state studied experimentally by diffraction in the work of Hensel *et al.* along the liquid–vapour coexistence curve of metallic fluid Cs. The reasons for this are exposed.

KEY WORDS: Ornstein-Zernike direct correlation function. Inverse problem.

The proposal of Johnson and March[1] to extract the pair potential $\phi(r)$ from diffraction data yielding the liquid structure factor $S(k)$ has been recently brought to full fruition for Na at the melting point by Reatto and coworkers[2–4]. Their potential has all the characteristics found in a subsequent, all electron, calculation on liquid Na by Perrot and March[5]. The work of Refs 2–4 demonstrates clearly that one approximate structural theory, the modified hypernetted chain (HNC) method, is not quantitative at the melting point of Na, and therefore must be refined by iteration using computer simulation.

Our interest here is in another, but heavier, alkali, Cs, and we have no reason to doubt that the same conclusion will obtain: namely that available approximate structural theories will not be sufficiently accurate for quantitative work at the melting point. However, Hensel and coworkers[6] have measured $S(k)$ at various thermodynamic states along the liquid–vapour coexistence curve. What will be shown below is that three approximate structural theories, applied to a low density state of Cs examined by Hensel *et al.*[6], all yield pair potentials $\phi(r)$ with common features, and the reasons for this will be exposed.

Let us take as starting point the approximate method proposed by de Angelis and March[7] for extracting the pair potential $\phi(r)$ from the measured structure factor $S(k)$ and the Fourier transform of $(S(k) - 1)$, namely $g(r) - 1$, with $g(r)$ the usual liquid pair function. Then, writing $g(r)$ for the ions, which may be treated classically, in the Boltzmann form

$$g(r) = \exp(-U(r)/k_B T) \tag{1}$$

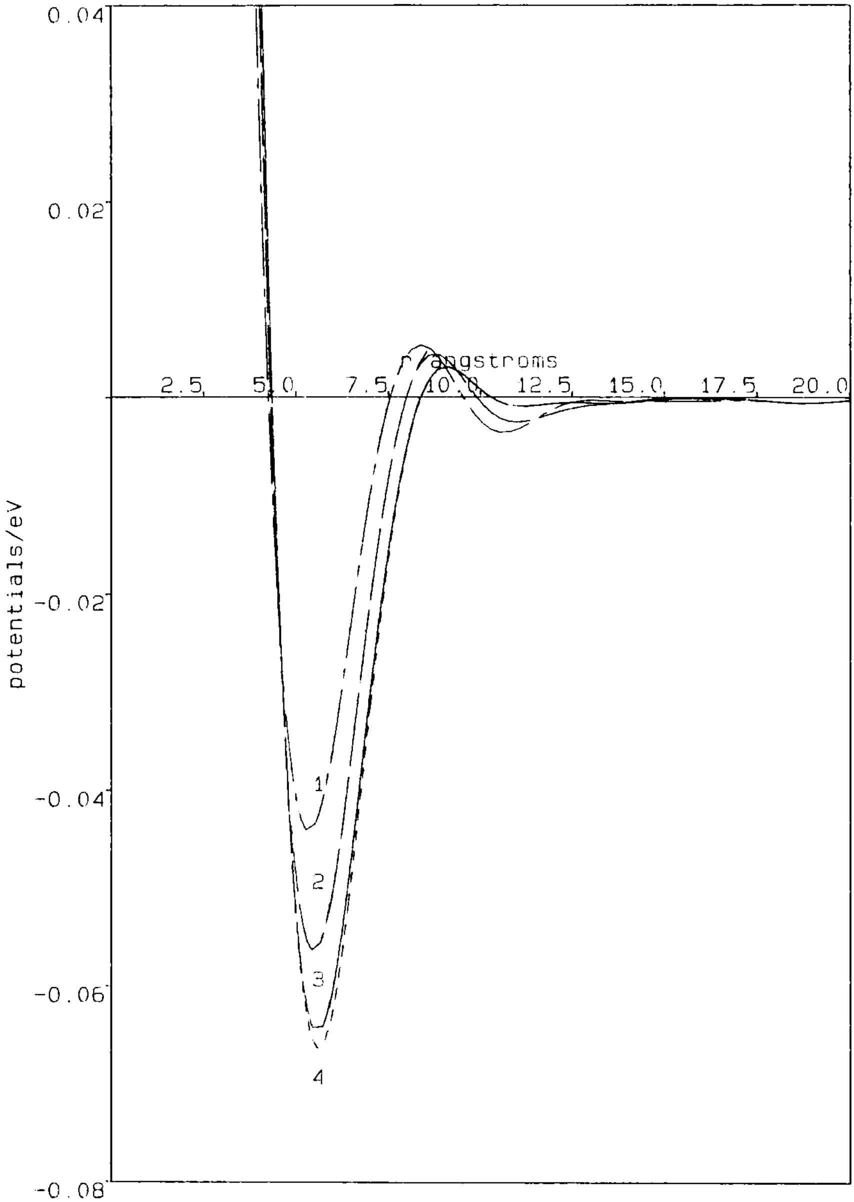

Figure 1 Curve 1. Potential of mean force $U(r)$ from experiment. This is for the thermodynamic state of fluid metallic Cs corresponding to density $\rho = 0.00416\ \text{Å}^{-3}$ and to temperature $T = 1923$ K. Curve 2. Pair potential $\phi(r)$ extracted from experiment via Eq. (2). Curve 3. $\phi(r)$ obtained from same data as used in curve 1, but via Eq. (3). Curve 4. $\phi(r)$ obtained using Percus–Yevick approximation[8].

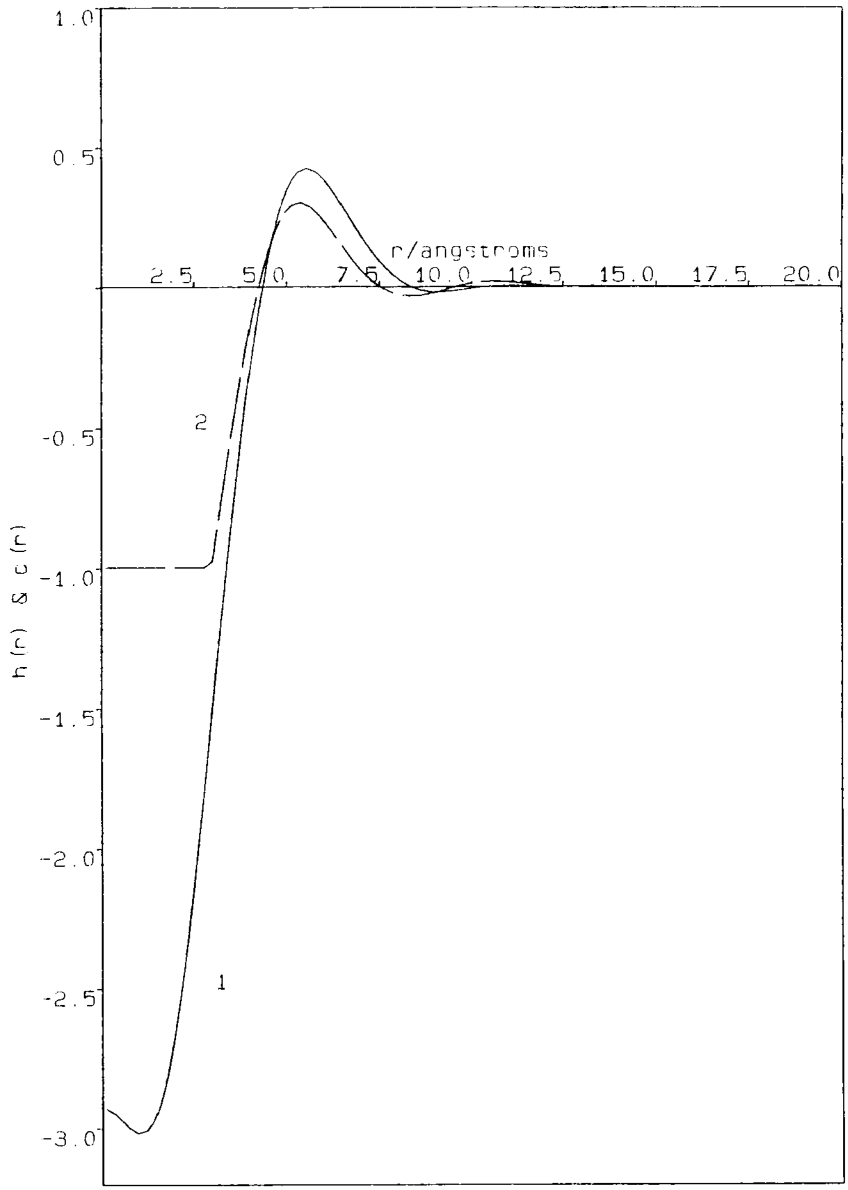

Figure 2 Curve 1. Ornstein–Zernike function for same state of fluid Cs as in Figure 1. This was calculated from diffraction data of Hensel and coworkers[6] by Fourier transform of $[S(k) - 1]/S(k)$. Curve 2. Shows total correlation function $h(r) = g(r) - 1$. This was calculated by Fourier transform of $[S(k) - 1]$, using again experimental data for the same thermodynamic state as in Figure 1.

the pair potential is related[7] to the potential of mean force $U(r)$ and the structure factor $S(k)$ by

$$\frac{\phi(r)}{k_B T} = \frac{U(r)}{k_B T} + \frac{1}{8\pi^3 \rho} \int [S(k) - 1]^2 \exp(i\mathbf{k} \cdot \mathbf{r})\, d\mathbf{k}, \tag{2}$$

where ρ is the number density of ions. For the thermodynamic state of liquid Cs specified, $U(r)$ in curve 1 of Figure 1 has been derived from $-k_B T \ln g(r)$ according to Eq. (1), with $g(r)$ obtained by Fourier transform of the data of Hensel *et al.*[6]. With this same data, $U(r)$, according to Eq. (2), has to be "corrected" by the Fourier transform of $[S(k) - 1]^2$. The resulting pair potential $\phi(r)$ is displayed in curve 2 of Figure 1.

The hypernetted chain (HNC) theory in its original form gives

$$\frac{\phi(r) - U(r)}{k_B T} = h(r) - c(r) \tag{3}$$

where the total correlation function $h(r)$ is simply $g(r) - 1$ while $c(r)$ is the usual Ornstein–Zernike direct correlation function. This latter function $c(r)$ is plotted in curve 1 of Figure 2, while the corresponding $h(r)$ is shown in curve 2. Using these results in Eq. (3), with the $U(r)$ already utilized in curve 1 of Figure 1, the corresponding pair potential is drawn in curve 3 of that Figure. There is seen to be good overall agreement between the potentials extracted using Eqs (2) and (3). Thirdly, we have studied the inversion of the Percus-Yevick (PY) approximation[8]; the result being shown in curve 4 of Figure 1.

While none of the three approximate theories used above can be expected to lead to a quantitatively reliable pair potential at the melting point of Cs, all of them evidently yield pair potentials $\phi(r)$ at the low density thermodynamic state considered here with common characteristics. After studying the details of the calculations for the three cases, the reason for the agreement is found to lie in the fact that, in the regions of **r** space important in determining the main characteristics of $\phi(r)$, the quantity $h - c$ is small compared with $h(r)$*, except of course very near the nodes of this latter quantity.

Finally, it needs stressing that, although this work has focussed only on a low density metallic state of Cs, closer approach to the critical point will lead eventually to a situation where the form of $g(r)$ becomes dominated by critical fluctuations rather than by the pair force law. The approximate theories employed above are not then rich enough to embrace this regime. Therefore the limited range of validity of the procedure proposed here must be borne in mind. We are currently engaged, with Mr. C. M. Allison, in setting up computer simulation to fully test the pair potentials $\phi(r)$ in Figure 1. When this simulation has been completed, a full account of this work will be published.

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* The weaker condition $|h - c|$ considerably less than unity leads to $\phi_{HNC}(r)$ in agreement with $\phi_{PY}(r)$.

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