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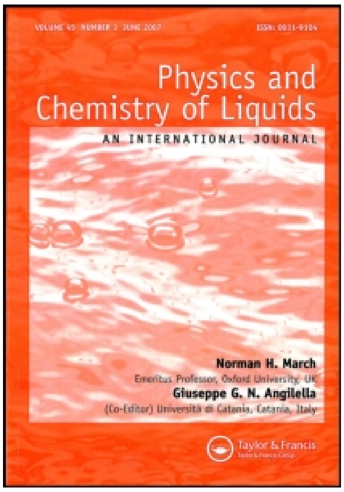

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Effective Pair Potentials Describing The Measured Structure Factor Of Expanded Caesium Near The Critical Point

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EFFECTIVE PAIR POTENTIALS DESCRIBING THE MEASURED STRUCTURE FACTOR OF EXPANDED CAESIUM NEAR THE CRITICAL POINT

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Some theoretical and computational works on expanded caesium near the critical point have been reported after Winter and Hensel's neutron diffraction experiments. Here we present effective pair potentials almost reproducing the observed structure data ($T = 1923$ K, $\rho = 0.59$ g/cm^3). In order to obtain such effective pair potentials we use four types of reference potentials: a hard-sphere potential, a hard-sphere Yukawa potential, a Lennard-Jones potential and a pair potential derived from the pseudopotential theory. The final effective pair potentials reconstructed in this work almost equally reproduce the observed structure factor of expanded caesium at 1923 K within the accuracy of the Percus–Yevick approximation. A molecular dynamics calculation is also presented in comparison with these results.

KEY WORDS: Expanded caesium, inverse problem, effective pair potential.

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1 INTRODUCTION

Recently Winter *et al.*[1–3] have investigated the structure of expanded liquid caesium (Cs) along the liquid-vapour coexisting curve by neutron scattering experiments and found some interesting characteristic features of density dependence of the structure factors. Very recently Nield *et al.*[4] have investigated the structure and electrical resistivity of expanded Cs at 1673 K using the reverse Monte Carlo method. Although this method is excellent in reproducing the structure of expanded Cs, information of pair potential can not be obtained without further approximations. On the other hand Hoshino *et al.*[5–7] have calculated, using effective pair potentials obtained by the pseudopotential theory, the structures of expanded liquid Cs in the modified hypernetted chain approximation (MHNC) and by the molecular dynamics (MD) method. These authors showed that their MD and MHNC results agree quite well with each other but do not agree well with the experimental observations near the critical region.

So far, many theoretical works[8–11] have been reported for expanded liquid Rb using the pseudopotential theory. However, when the density becomes lower the structural disagreement between theory and experiment becomes clear, especially in the low-wavenumber-k region in the structure factors. As the metal-nonmetal transition is approached, mean free path of a conduction electron will be as short as the average interatomic distance and the nearly-free electron model within the framework of the linear screening theory is questionable to describe the strong thermodynamic state dependence of the effective interatomic interactions. In the light of this situation we try to extract effective pair potentials from the elaborate diffraction data near the critical point using four different types of reference potentials. A procedure[12,13] is now available, even at the critical point, for the inversion problem of structure data that is quantitatively reliable, given really accurate experimental structure data over a wide range of wavenumber k including, in a very essential way, small-angle scattering data. In the present work the four types of the reference potentials we employ do not have important physical meaning. These are chosen only for the purpose of reproducing the diffraction data in the high-k region.

The aim of this paper is to present the effective pair potentials for Cs which almost reproduce the observed structure data ($T = 1923$ K, $\rho = 0.59$ g/cm^3) closest to the critical point and to show a striking feature played by the tail part of the effective pair potentials. We have learned quite recently the work of Ascough and March[14] on the effective pair potentials deduced from the same diffraction data of expanded Cs. Therefore it is quite interesting to compare the results obtained by the two different approaches to the same problem.

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2 THE MODEL

We suppose that an effective pair potential $v_{\text{eff}}(r)$ can be divided into two parts[12,15]:

$$v_{\text{eff}}(r) = v_{\text{ref}}(r) + v_{\text{tail}}(r) \tag{1}$$

where $v_{\text{ref}}(r)$ denotes a reference potential describing diffraction data from the first-peak region to high k and $v_{\text{tail}}(r)$ denotes the tail potential which is responsible for modifications of the structure factor at small k. Thus once a $v_{\text{ref}}(r)$ is determined to reproduce the diffraction data from the first-peak region to high k, the $v_{\text{tail}}(r)$ is evaluated from the small-angle part of the diffraction data as

$$v_{\text{tail}}(r) = \frac{k_B T}{(2\pi)^3 n} \int_0^\infty \left(\frac{1}{S_{\text{expt}}(k)} - \frac{1}{S_{\text{ref}}(k)} \right) \frac{\sin kr}{kr} 4\pi k^2 \, dk \tag{2}$$

where n is the number density of ions, and $S_{\text{expt}}(k)$ and $S_{\text{ref}}(k)$ are respectively, the experimental structure factor and the reference structure factor corresponding to the $v_{\text{ref}}(r)$. In the previous works the upper limit of the integral was terminated by $k_0 = (18\pi^2 n)^{1/3}$. This is a very good approximation when $S_{\text{ref}}(k)$ merges into $S_{\text{expt}}(k)$ around the wavenumber k_0[15]. In the case of expanded Cs for 1923 K, however, this is not the case and we extended the limit to $3k_0$. Of course, the fit between $S_{\text{expt}}(k)$ and $S_{\text{ref}}(k)$ for $k > 3k_0$ is not perfect because we have a sum rule:

$$\int_0^\infty (S_{\text{expt}}(k) - S_{\text{ref}}(k)) 4\pi k^2 \, dk = 0. \tag{3}$$

However, we shall neglect any imperfection in the fit in this region and concentrate on the k-region lower than $3k_0$.

3 PROCEDURE

We employ the following four types of reference potentials in order to describe the diffraction data from the first-peak region to high k. The values of the parameters characterizing these potentials are determined to meet this requirement.

i) Hard-sphere potential;

$$\begin{aligned} v_{\mathrm{ref}}^{\mathrm{HS}}(r) &= \infty \quad \text{for} \quad r < \sigma^{\mathrm{HS}}, \\ &= 0 \quad \text{for} \quad r \geq \sigma^{\mathrm{HS}} \end{aligned}$$

where σ^{HS} is the diameter of the hard sphere. $\sigma^{\mathrm{HS}} = 3.75$ Å (the corresponding packing fraction $\eta = 0.074$) is used in this work.

ii) Hard-sphere Yukawa potential;

$$\begin{aligned} v_{\mathrm{ref}}^{\mathrm{HSY}}(r) &= \infty \quad \text{for } r < \sigma^{\mathrm{HSY}}, \\ &= \mathrm{k_B} T\gamma\sigma^{\mathrm{HSY}}/r \exp(\alpha r/\sigma^{\mathrm{HSY}}) \quad \text{for } r \geq \sigma^{\mathrm{HSY}} \end{aligned}$$

where σ^{HSY} is the diameter of the hard-sphere, γ is the scaled strength of the Yukawa interaction at hard contact and α is the scaled inverse screening length. $\sigma^{\mathrm{HSY}} = 3.16$ Å, $\gamma = 80$ and $\alpha = 3.5$ are used in the present work.

iii) Lennard-Jones potential;

$$v_{\mathrm{ref}}^{\mathrm{LJ}}(r) = 4\varepsilon[(\sigma^{\mathrm{LJ}}/r)^{12} - (\sigma^{\mathrm{LJ}}/r)^{6}]$$

where σ^{LJ} is the atomic collision diameter and ε is the minimum potential energy. $\sigma^{\mathrm{LJ}} = 4.57$ Å and $\varepsilon = 185.3\ \mathrm{k_B}T$ are used in this work.

iv) Pair potential derived from the pseudopotential theory (in atomic units)[16,17];

$$v_{\mathrm{ref}}^{\mathrm{PS}}(r) = \frac{Z^2}{r}\left(1 - \frac{2}{\pi}\int_0^\infty \frac{F_{\mathrm{N}}(k)}{k} \sin kr \, \mathrm{d}k\right)$$

where Z is the valence and

$$F_{\mathrm{N}}(k) = \left(\frac{k^2 v(k)}{4\pi Z}\right)^2\left(1 - \frac{1}{\varepsilon(k, n)}\right)$$

is the normalized energy-wavenumber characteristic. $v(k)$ is the local pseudopotential and $\varepsilon(k, n)$ is the screening function. We employ the Ashcroft empty-core form

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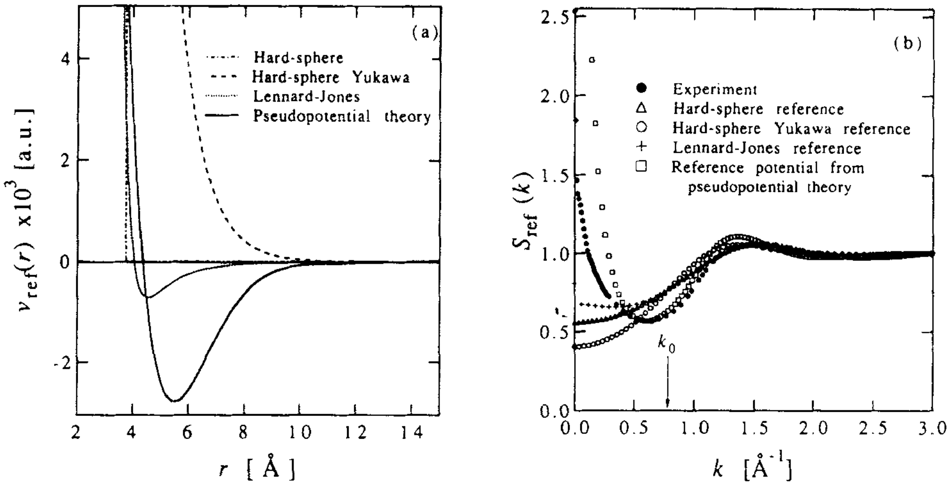

Figure 1 Reference potentials $v_{ref}(r)$ and corresponding structure factors $S_{ref}(k)$.

$v(k) = -(4\pi Z/k^2)\cos kr_c$ for the pseudopotential with r_c being the core radius, and the Geldart–Vosko[18] expression to describe the electron gas. $Z = 0.9$, $r_c = 2.60$ a.u. and $\rho = 0.80$ g/cm^3 are used in the present work. We treat density and valence as parameters so as to avoid a divergent behaviour of $S(k)$ in the long wavelength region.

4 RESULTS

Figure 1(a) shows the four types of the reference potentials which are quite different in shape from each other. With these reference potentials the corresponding structure factors $S_{ref}(k)$ are, except for the HS Yukawa case[19], calculated using the PY integral equation. These results are displayed in Figure 1(b) and compared with the experimental data[20]. As can be seen from this figure, the observed $S_{expt}(k)$ beyond $k = 1.13$ Å^{-1} is well described by these reference potentials. In the lower-k region any of these reference potentials does not describe the observed data: the potentials (i), (ii) and (iii) underestimate the observed density fluctuations, while the potential (iv) overestimates the latter.

As is mentioned at the end of the previous section, the reference potential derived from the pseudopotential theory causes some difficulty in the structure calculations. We want to present such difficulty arising from the usual usage of the pseudopotential-derived-pair potential.

Figure 2(a) shows the two types of reference potentials for Cs. The potential of type 1 is obtained by using the valence $Z = 1.0$ and the measured density $\rho = 0.59$ g/cm^3 at $T = 1923$ K, whereas that of type 2 is obtained by using $Z = 0.9$ and $\rho = 0.80$ g/cm^3. The empty-core radius $r_c = 2.60$ a.u. is uniquely determined by the density of liquid Cs near the melting point[21] and is used in the two potentials. The potential of type 2 is employed as the reference potential throughout this work. If

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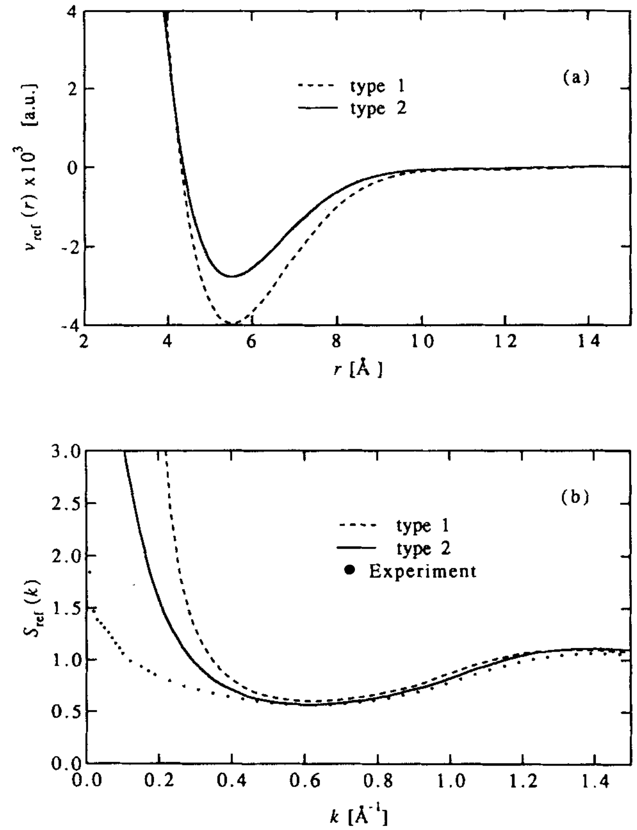

Figure 2 Two types of the reference pair potentials $v_{ref}(r)$ derived from the pseudopotential theory and corresponding structure factors $S_{ref}(k)$. Type 1: $\rho = 0.59$ g/cm^3, $Z = 1.0$, $r_c = 2.60$ (a.u.); type 2: $\rho = 0.80$ g/cm^3, $Z = 0.9$, $r_c = 2.60$ (a.u.).

we use the potential of type 1 as a reference potential it is difficult to obtain a good convergence of PY solution, which leads to a divergent behaviour of $S(k)$ in the long wavelength region. This is illustrated in Figure 2(b). Furthermore, if we use the potential of type 1 in the MD simulations we find that a clustering of ions occurs and no reasonable pair distribution function is obtained. The reason is that the potential of type 1 is too attractive and binds the ions too strongly. This can be corrected by choosing the valence and the density as the potential of type 2. The correction makes the reference potential less repulsive and less attractive as is evidently shown in Figure 2(a). The choice of $Z = 0.9$ and $\rho = 0.8$ g/cm^3 is made only for avoiding the divergence of $S(k)$ in the low-k region.

Now tail potentials $v_{tail}(r)$ are evaluated from the difference between the calculated $S_{ref}(k)$ and $S_{expt}(k)$, and then added to the $v_{ref}(r)$ to obtain the effective pair potentials $v_{eff}(r)$. The $v_{eff}(r)$ thus obtained are shown in Figure 3(a). Surprisingly, the quite-different-four-type $v_{ref}(r)$ predicts quite similar $v_{eff}(r)$. Furthermore, the four $v_{eff}(r)$ are

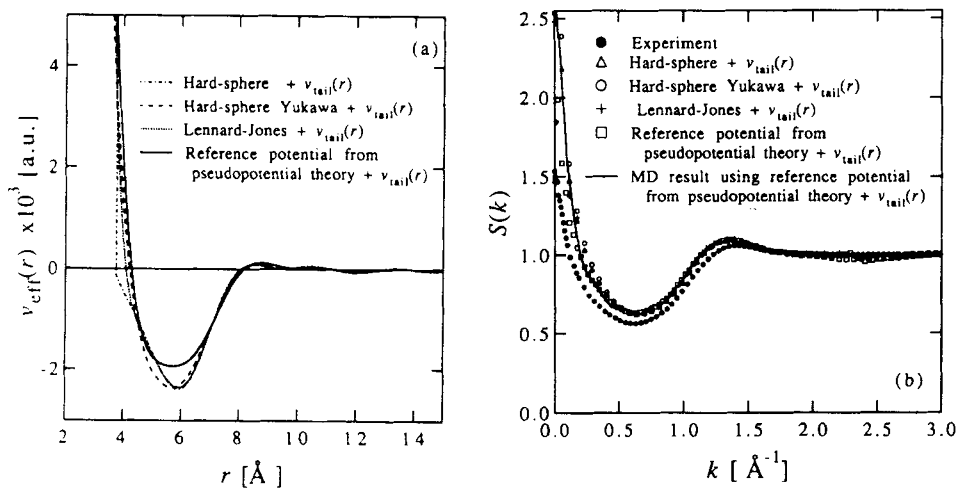

Figure 3 Effective pair potentials $v_{eff}(r)$ and corresponding structure factors $S(k)$. The tail potential $v_{tail}(r)$ obtained by Eq. (2) depends on the reference potential employed. $S_{expt}(0) = 2.54$ and $S_{MD}(0) = 2.99$.

much the same as far as the attractive part is concerned. Thus our interest is focused on the following question. Do our potentials reproduce the low-k diffraction data by which these potentials are extracted? With these $v_{eff}(r)$ the corresponding structure factors $S(k)$ are again calculated using the PY integral equation. The results are shown

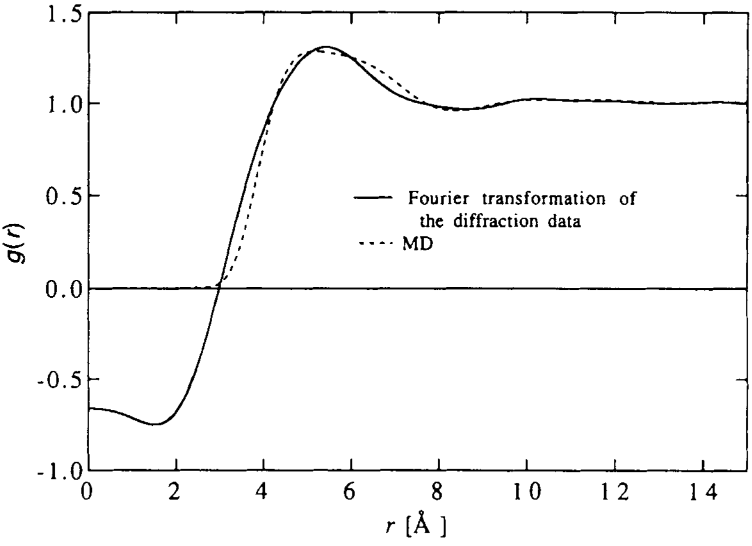

Figure 4 Pair distribution functions $g(r)$ of expanded Cs near the critical point.

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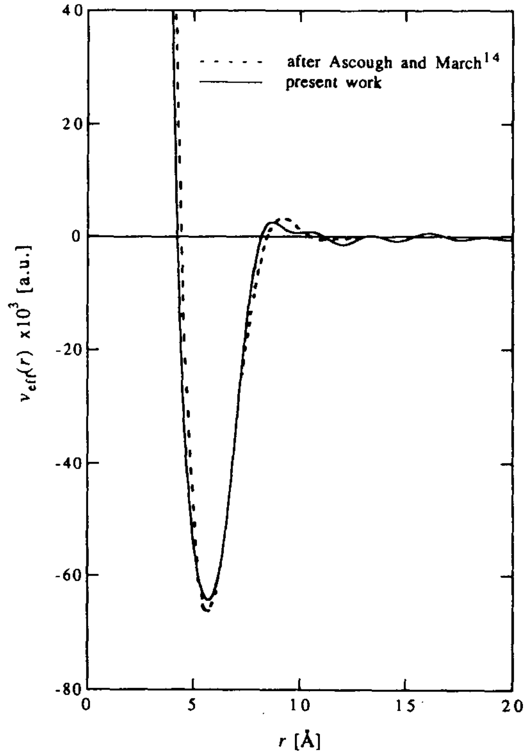

Figure 5 Comparison of one of the present pair potentials (Hard-sphere Yukawa + $v_{\text{tail}}(r)$) with one of those (curve 4 obtained using the Percus–Yevick approximation) of Ref. 14. The present potential shown in Figure 5 is in excellent agreement with curve 3 of Ref. 14.

in Figure 3(b). As can be seen from this figure our $v_{\text{eff}}(r)$ almost equally reproduce the $S_{\text{expt}}(k)$ of expanded Cs at 1923 K, although the calculated $S(k)$ are slightly higher than the $S_{\text{expt}}(k)$ over the whole range of k of interest. The present results obviously demonstrate that the $v_{\text{tail}}(r)$ is essential for reproducing the observed density fluctuations and that this is fully evaluated from Eq. (2).

MD calculations have been carried out, using the reference potential from the pseudopotential theory and $v_{\text{tail}}(r)$, to calculate the pair distribution function $g(r)$. The $S(k)$ obtained by Fourier transformation of the $g(r)$ is also shown in Figure 3(b) in comparison with the PY results. Agreement between the two is very good as is seen from the figure. The $g(r)$ obtained from Fourier transformation of the diffraction data is displayed in Figure 4 together with that from the MD simulation. The former exhibits an unphysical negative portion in the small-r region which is caused by the lack of the experimental structure data in the high-k region. The agreement between the two sets of the $g(r)$ is rather good in the large-r region beyond ~7.5 Å, although there exist some discrepancies in the first-peak region.

5 DISCUSSION

Quite recently Ascough and March[14] have reported in this journal that three approximate structural theories (hypernetted chain, Percus–Yevick and Angelis-March approximations), applied to a low density state of Cs examined by Hensel *et al.*, all yield pair potentials with common features. What is instructive is that while none of the three approximate theories used by those authors can be expected to lead to a quantitatively reliable pair potential at the melting point of Cs, all of them evidently yield the pair potentials with common characteristics at the low density thermodynamic state. The present work strongly supports their proposition in this respect. Figure 5 shows comparison of one of our potentials with one of those of Ref. 14. Evidently, there is seen to be good agreement between ours and theirs, although small differences can be seen in the depth of the potential as well as in the region of the main hump of the potential. It should be stressed that the curvature of both sides of our potential wall is quite similar to theirs and this is responsible for describing the diffraction data in the whole range of k (see Figures 3(a) and 3(b)). The close similarity between our potential and the Ascough-March potential appears to give a clue toward elucidation of the pair interaction at the low density metallic state of Cs.

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6 CONCLUSIONS

The conclusions drawn from the present study are as follows:

1) The tail part of the effective pair potential $v_{\mathrm{tail}}(r)$ is essential to reproduce the observed density fluctuations in the low-k region.

2) The $v_{\mathrm{tail}}(r)$ is well evaluated from the small-angle part of the diffraction data using Eq. (2).

3) The present work supports Ascough-March's view that pair potentials with common features are extracted from the inversion of the diffraction data at a low density state of Cs.

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