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Effective Interatomic Pair-Potentials in Liquid Alkali Metals via the RPA and MC Simulation Methods

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A useful method which is based on the RPA and Monte Carlo computer simulation is presented for calculating an effective interatomic pair-potential from an observed structure factor. The method is applied to liquid Na, K, Rb and Cs and gives reliable pair-potentials compatible with the predictions of the pseudopotential theory. The lack of elaborate scattering experiments, however, seriously limits the use of the present method in extracting a reliable effective pair-potential.

1 INTRODUCTION

The direct determination of the effective pair-potential $v_{\text{eff}}(r)$ from the measured structure factor $a(k)$ of a liquid has been a continuing interest since the pioneering works of March and coworkers.^{1,2} So far, many different schemes, all approximate to some degree, have been proposed for this purpose; for a very recent discussion, see, for example, Ailawadi.³ Among these we particularly refer to the most recent works of Olsson and Dahlborg⁴ on the one hand, and McLaughlin and Young⁵ on the other. The former used an extended version of the random phase approximation (RPA) developed by Gaskell,⁶ whereas the latter employed the ordinary RPA formula combining features of the modified WCA developed by Jacob and Andersen.⁷

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The aim of the present investigation is to show the usefulness of the two approaches and to comment on the $v_{\text{eff}}(r)$ in alkali metals using the Monte Carlo (MC) computer simulation results obtained by Hansen and Schiff (HS).

We suppose that the total effective pair-potential $v_{\text{eff}}(r)$ can be divided into two parts:

$$v_{\text{eff}}(r) = v_{\text{core}}(r) + v_{\text{tail}}(r), \quad (1)$$

where $v_{\text{core}}(r)$ denotes a positive repulsive potential to represent the core and $v_{\text{tail}}(r)$ denotes the tail potential which is, from the RPA formula, given by

$$v_{\text{tail}}(r) = \frac{k_B T}{(2\pi)^3 \rho} \int_0^\infty \left[\frac{1}{a(k)} - \frac{1}{a_{\text{core}}(k)} \right] \frac{\sin kr}{kr} 4\pi k^2 dk, \quad (2)$$

ρ being the ionic number density. In Eq. (1) $v_{\text{core}}(r)$ is responsible for the structure factor at large k and $v_{\text{tail}}(r)$ for modifications at small k . McLaughlin and Young characterized $v_{\text{core}}(r)$ so that a modified WCA calculation yields a structure factor $a_{\text{core}}(r)$ such that $a_{\text{core}}(k) \approx a(k)$ at large k . For the liquid metals such as Al, In and Pb they used the core part of the interatomic potential obtained by Ascroft pseudopotentials⁹ and Vashishta-Singwi screening theory.¹⁰ As Olsson and Dahlborg, however, have pointed out in their paper thorough MC computations by HS, applying various repulsive interatomic potentials, clearly indicate the importance of the repulsive forces on $a(k)$ even at small k as we also see later. Moreover, the modified WCA method appears to be accurate for ‘softness parameter’ $\rho \cdot B(\pi/\sigma) \lesssim 0.15$, $B(k)$ being the Fourier transform of the ‘blip’ function, which includes many liquid metals but not the alkalis.

In the present work we have used the RPA method employing the MC simulation results in describing $v_{\text{core}}(r)$. The thermodynamic properties of systems of particles interacting through an inverse power potential $V(r) = \varepsilon(\sigma/r)^n$, and particularly the fluid-solid phase transition of such systems, have been studied through computer ‘experiments’ by Hoover *et al.*¹¹ and by Hansen.¹² This is followed by HS who have studied and compared the radial distribution functions and liquid structure factors at crystallization (freezing) for the cases $n = 12, 9, 6, 4$ and 1 , respectively. In the present studies we confine ourselves to the cases $n = 12, 9, 6$ and 4 , excluding the two extreme cases of hard spheres and of the one-component plasma at solidification.

In order to see whether this approach is any better than the other approximations proposed up to now, we first study liquid Rb at 319K and a density of $1.502 \text{ g} \cdot \text{cm}^{-3}$, and then liquid Na, K and Cs, at the melting points for the following reasons: (i) Using a given pair-potential, a molecular dynamics (MD) calculation has been performed by Rahman¹³ for liquid Rb at the temperature and density above. The use of the MD data on the structure

factor for liquid Rb thus provides a rigorous test of our ideas, in that any deviation from the input pair-potential is directly attributable to the inadequacies in the present approach; (ii) Experimental structure factor data on liquid Na, K and Cs have been widely used by several authors so as to calculate pair-potentials from various approximate methods. Our results can, therefore, be easily compared with either those of the approximate theories or those based on the pseudo-potential formalism reported so far.

2 RESULTS AND DISCUSSIONS

First of all, in Figure 1, we show that structure factor data of HS for $n = 12, 9, 6$ and 4 together with that of Raman for liquid Rb at the temperature and density mentioned above. As is seen from the figure, at low k -region (up to $k\sigma \approx 4$) the MC results are considerably lower than that of Rahman, merging with the latter at around $k_0 = 3^{1/3}k_D$ where k_D is the radius of the conventional Debye sphere. Beyond k_0 Rahman's $a(k)$ data are well reproduced by the MC results except for the region of the first peak in $a(k)$ for $n = 4$. With a hard-core calculation it is sometimes possible (Young,¹⁴ Bristol Confer. Figure 3, and March and Tosi,¹⁵ Figure 2.9) to reproduce a fit of the type shown in Figure 1. Of course, the fit for $k \gtrsim k_0$ is not perfect since, for example, we have a sum rule:

$$\int_0^{\infty} [a_{\text{expt}}(k) - a_{\text{core}}(k)] 4\pi k^2 dk = 0. \quad (3)$$

However, we shall neglect any imperfection in the fit in this region and concentrate instead on the lower k , larger r regions. We believe this is the basic idea of the McLaughlin and Young method. The corresponding effective pair-potentials $v_{\text{eff}}(r)$ obtained through Eqs. (1) and (2) are displayed in Figure 2 along with those found via pseudopotential theories.^{16,17} The broken curve shows the potential $\varphi_p(r)$ of Price *et al.*¹⁷ that was used by Rahman to produce $a(k)$ through the MD simulation and is the result that should be ideally recovered from the present approach. From Figure 2 it is clear that the $\varphi_p(r)$ is semiquantitatively well reproduced by $a_{\text{core}}(k)$ for $n = 6, 9$ and 12 . Their trends relative to the $\varphi_p(r)$ are as follows. The r^{-6} case gives a right size of depth and position of the first minimum, while the r^{-12} case gives a little deeper and shifted position of the first minimum. As for the r^{-9} case we expected a curve falls between the r^{-6} and r^{-12} cases, but this is not so and different in behaviour from the former. For the r^{-4} case, on the other hand, no reasonable shape of $v_{\text{eff}}(r)$ has been obtained. Before going into more detailed considerations on Rb, we next present the results for liquid Na, K and Cs, which are shown in Figures 3–8. As is easily seen from

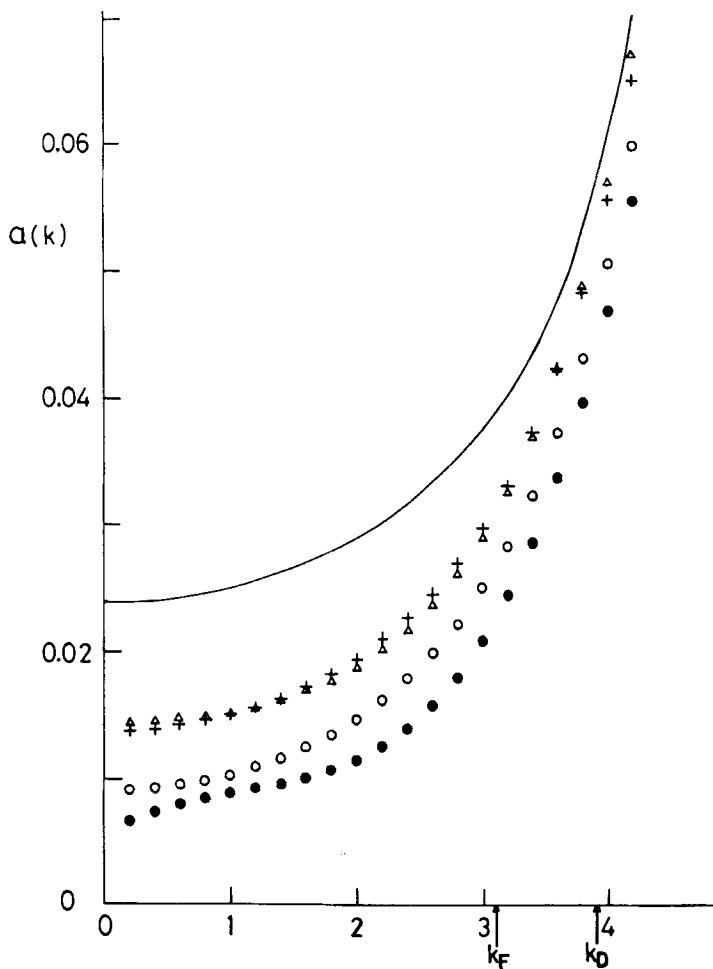


FIGURE 1(a) Structure factors at small k -region. The solid line denotes Rahman's $a(k)^{13}$ for liquid Rb at 319K and a density of $1.502 \text{ g} \cdot \text{cm}^{-3}$; the unit of length σ is chosen such that the experimental density is $1 \text{ ion}/\sigma^3$. The MC results are shown with +: $n = 12$, Δ : $n = 9$, O: $n = 6$ and \bullet : $n = 4$, taken from Hansen and Schiff.⁸

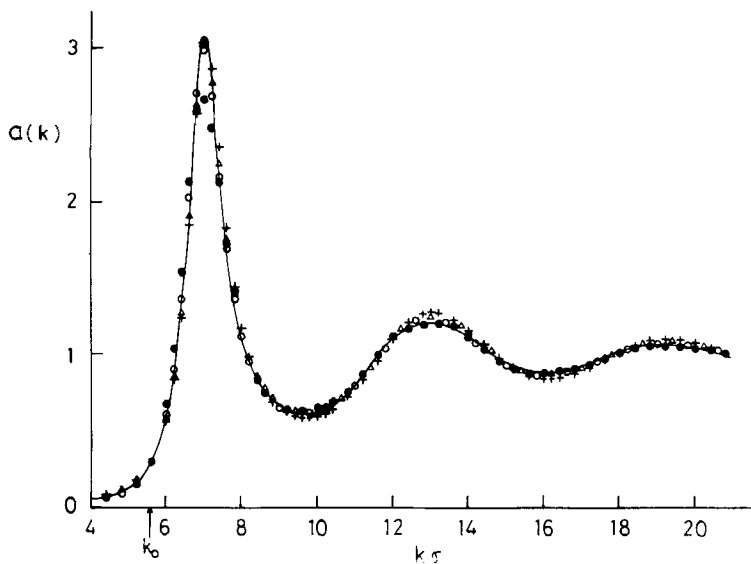


FIGURE 1(b) As Figure 1(a), for structure factors below the first peak to high k -region.

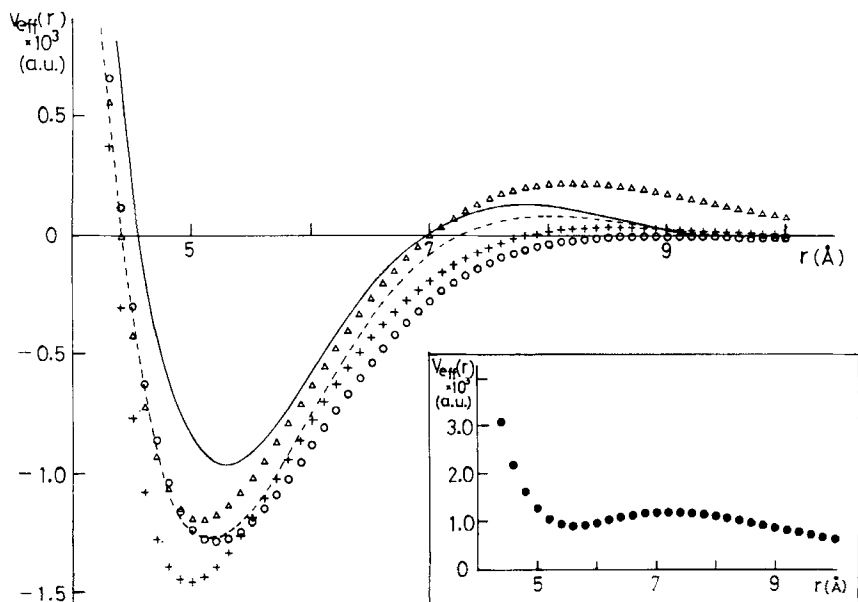


FIGURE 2 Effective pair-potentials corresponding to the structure factors mentioned in Figure 1. The insert shows the r^{-4} case. The solid line denotes the pair-potential of Bratkovsky *et al.*¹⁶, while the broken line denotes that of Price *et al.*¹⁷ which was used by Rahman to produce $a(k)$ shown in Figure 1.

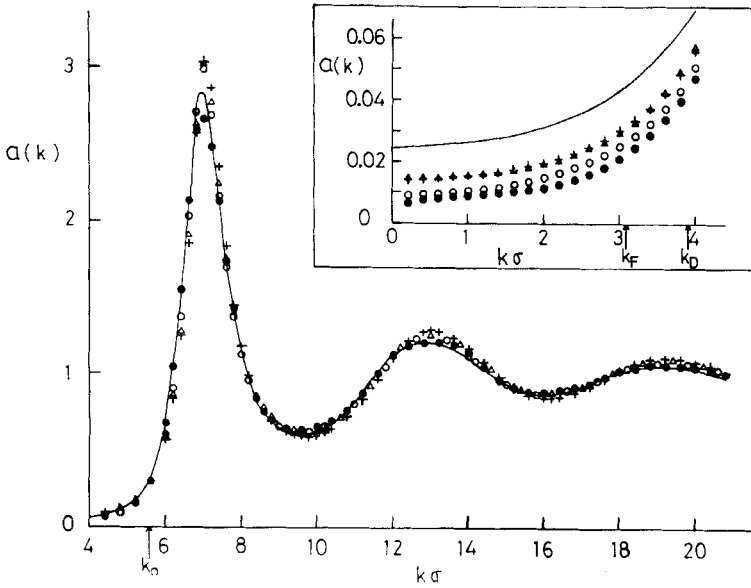


FIGURE 3 As Figure 1, for liquid Na at 373K. The solid line denotes the observed $a(k)$ of Greenfield *et al.*¹⁸; the unit of length σ is chosen such that the experimental density is 1 ion/ σ^3 .

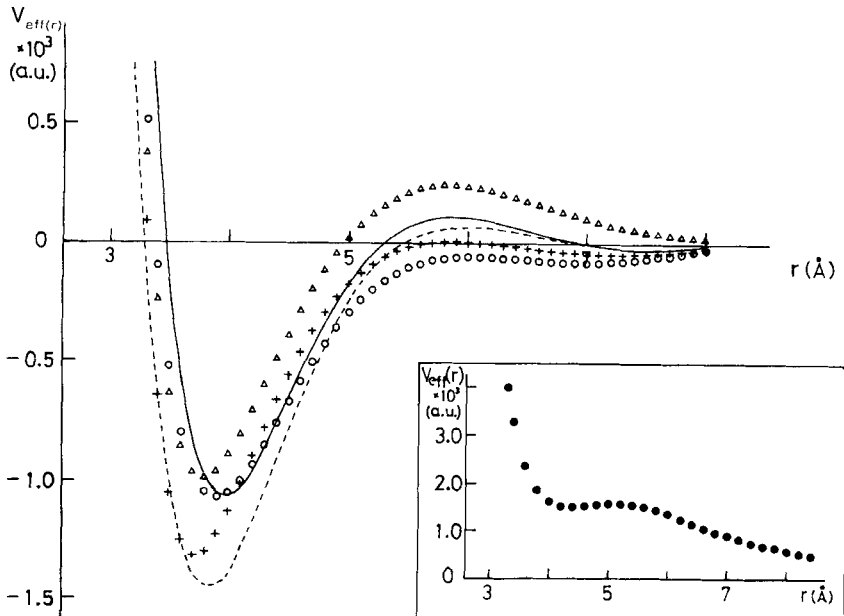


FIGURE 4 As Figure 2, for liquid Na at 373K; solid line: from Bratkovsky *et al.*¹⁶, broken line: from Price *et al.*¹⁷

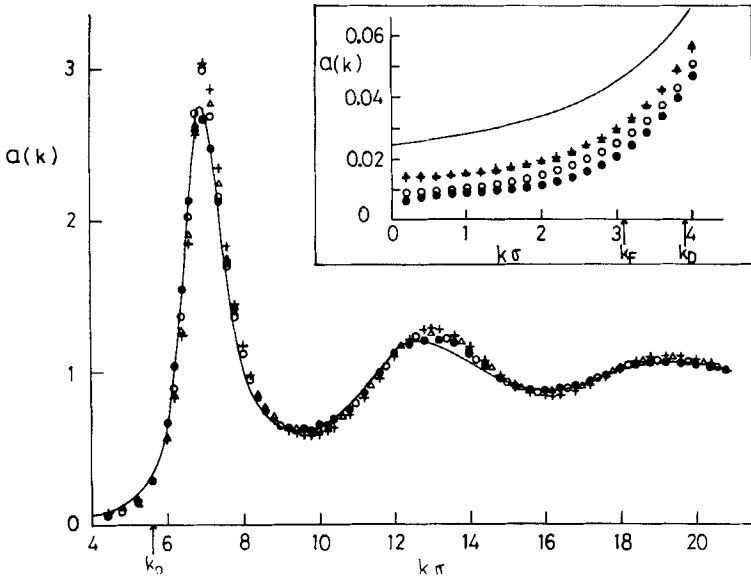


FIGURE 5 As Figure 1, for liquid K at 338K. The solid line denotes the observed $a(k)$ of Greenfield *et al.*; the unit of length σ is chosen such that the experimental density is $1 \text{ ion}/\sigma^3$.

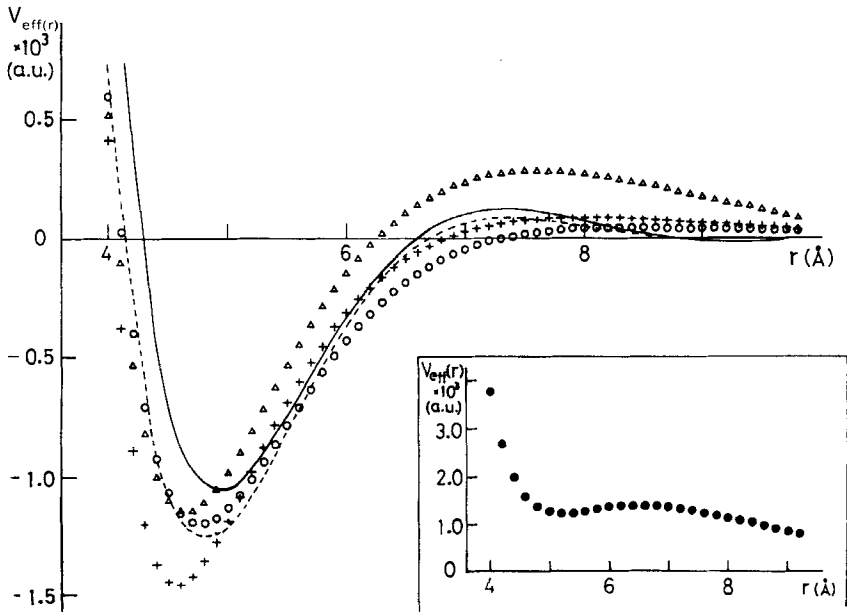


FIGURE 6 As figure 2, for liquid K at 338K; solid line: from Bratkovsky *et al.*,¹⁹ broken line: from Price *et al.*²⁰ ($m^*/m = 0.89, r_c = 2.45$).

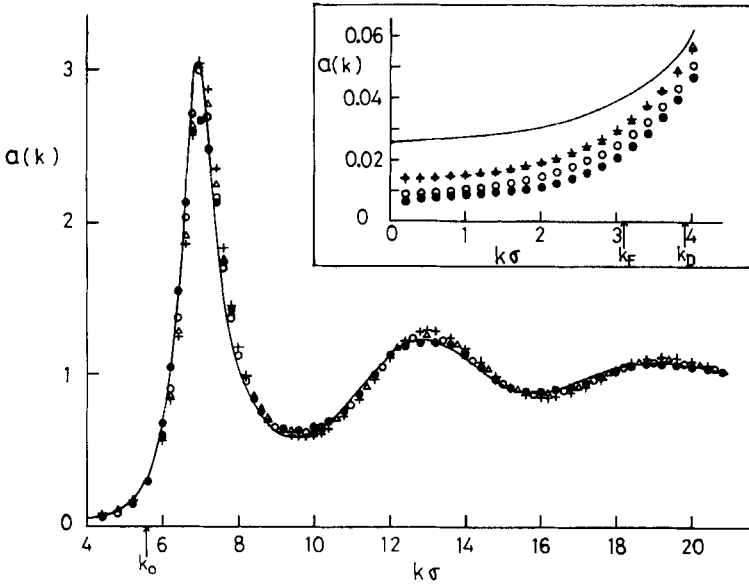


FIGURE 7 As Figure 1, for liquid C_6 at 303K. The solid line denotes the observed $a(k)$ of Huijben *et al.*²¹; the unit of length σ is chosen such that the experimental density is $1 \text{ ion}/\sigma^3$.

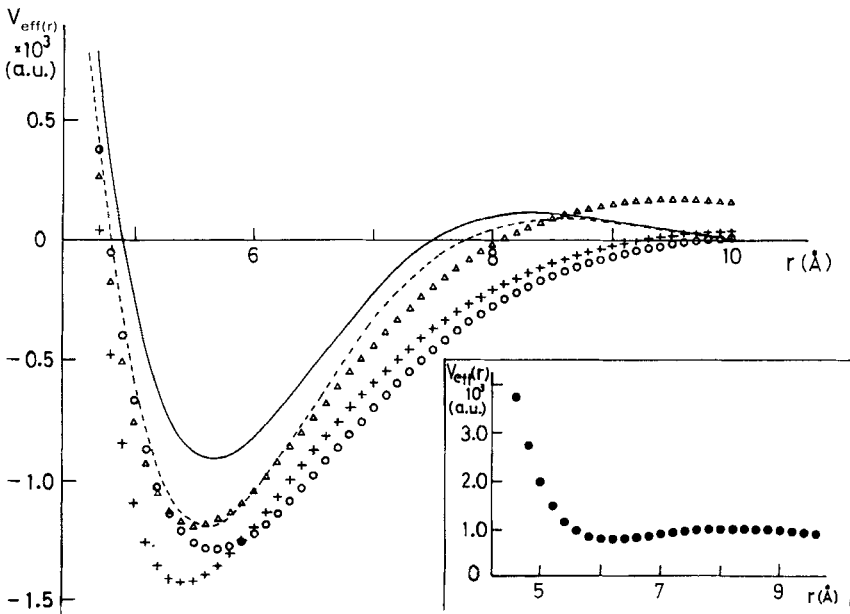


FIGURE 8 As Figure 2, for liquid C_D at 303K; solid line: from Bratkovsky *et al.*,¹⁹ broken line: from Price *et al.*²⁰ ($m^*/m = 0.85, r_c = 2.65$).

these figures the general features which we found in Rb have been well preserved in both the structure factors and the effective pair-potentials. Firstly at low k -region (up to about $k\sigma \approx 4$) the MC $a(k)$ are substantially lower than the observed $a(k)$, then merging with the latter at around k_0 . Beyond k_0 the observed $a(k)$ are moderately well reproduced by the MC $a(k)$ except for around the first and second peaks†. Secondly the calculated $v_{\text{eff}}(r)$ beyond the first minimum are quite similar in shape for both the r^{-6} and the r^{-12} cases, but not so for the r^{-9} case. Thirdly the 'size of core' of the $v_{\text{eff}}(r)$ gets slightly smaller with increasing n , and the depth of the $v_{\text{eff}}(r)$ gets slightly smaller with increasing n , and the depth of the $v_{\text{eff}}(r)$ gets deeper and shifts inwards in sequence except for the case of $n = 9$. Fourthly, no reasonable shape of the $v_{\text{eff}}(r)$ has been obtained for the r^{-4} case for each metal.

Now we are in a position to interpret these interesting results. So let us return to the paper of HS. As is well known in a computer simulation, the radial distribution function $g(r)$ can only be calculated to some finite value of r , the truncation of $g(r)$ at this point can lead to serious errors in $a(k)$ at small k . In order to avoid errors in the Fourier transform due to a truncation of $g(r)$ HS have extrapolated $g(r)$ by assuming the validity of the Percus-Yevick equation (see Hansen and Schiff,⁸ and the literature therein). According to them, in the two cases $n = 4$ and $n = 1$, the constant in Eq. (2) in their paper has been determined with an accuracy of only a few percent. Hence the $g(r)$ for these two potentials may not correspond exactly to the fluid at crystallization; this implies a somewhat larger uncertainty on the $g(r)$ and thence $a(k)$ values quoted for these potentials. Therefore, judging from Table III in their paper as well as the calculated $v_{\text{eff}}(r)$ for the r^{-4} case both the r^{-6} and the r^{-12} cases seem to be the most reliable in accuracy in describing $v_{\text{core}}(r)$. As stated in the previous section the input pair-potential should be recovered if the present approach is exact. In this sense we prefer the r^{-6} case as a description of $v_{\text{core}}(r)$ we confine ourselves to this case in the discussions below. Agreement between ours and the $\varphi_p(r)$ in Figure 2 is excellent up to the first minimum beyond which the former is considerably lower than the latter. Our question here is of where this discrepancy comes from, i.e., either from the RPA itself or from the MC $a(k)$. The RPA, however, should hold for $k \ll k_D$, which corresponds to $r \gg 1/k_D \approx 1.2 \text{ \AA}$ for liquid Rb near the melting point. Therefore a possible cause for this discrepancy lies in the MC $a(k)$ at small k . If so, do small corrections in $a(k)$ in this region reproduce exactly the $\varphi_p(r)$? To answer this question, let us try

† As far as the second peaks for Na and K are concerned the observed $a(k)$ data of Greenfield *et al.*¹⁸ are questionable in accuracy. If we use those of Huijben *et al.*²¹ the discrepancies between the MC and the observed $a(k)$ are removed. The calculated $v_{\text{eff}}(r)$, however, are little affected by imperfect fits around this region.

an arbitrary variation in the MC $a(k)$ up to about k_F and see what effect this has on the calculated potential. Numerical examples of such variations are given in Table I for explanatory purposes, and the corresponding $v_{\text{eff}}(r)$ are shown in Figure 9(a). With these numerical tests we found that only small upward corrections in the MC $a(k)$ in the range $0 \lesssim k\sigma \lesssim 1.4$ (case I) raise slightly the $v_{\text{eff}}(r)$ as a whole, whereas small downward modifications in the range $1.8 \lesssim k\sigma \lesssim 3$ (case II) lower slightly the $v_{\text{eff}}(r)$ in the region up to 6 \AA , though raising it a little from this point onward. The combination of case I with case II leads to case III which reproduces faithfully the $\varphi_P(r)$ up to the first hump, though giving somewhat exaggerated oscillation at larger r . In the end we learnt that errors in the MC $a(k)$ up to about k_F are mainly responsible for reproduction of the attractive part of the $\varphi_P(r)$.

Next we turn to the discussion connected with pseudopotential theory using the modified MC $a(k)$ labelled case III. The effective pair-potential $v_{\text{eff}}(r)$ as found from the observed $a(k)$ is often different from that $v_{PS}(r)$ calculated via pseudopotential perturbation theory. So far many calculated $v_{PS}(r)$ have been reported by a number of authors. The form of the $v_{PS}(r)$, however, is very sensitive to approximations used in the electronic screening calculation as well as the choice of the pseudopotential. So it appears still difficult to settle what approximation is really accurate for describing systematically the $v_{PS}(r)$ of simple liquid metals. Bearing this in mind, here we choose, for comparison, the most recent works of Bratkovsky *et al.*^{16,19} on the one hand, and the time-honoured ones of Price *et al.*^{17,20} on the other. Such a comparison is made in Figure 9(b), (c) and (d). For liquid Na, the present result is very similar to that of Bratkovsky *et al.* with somewhat small 'size of core' and slightly high attractive part at larger r . As for liquid K the repulsive part of the $v_{\text{eff}}(r)$ is in remarkably good agreement with that of

TABLE I

The original and the modified MC $a(k)$, for the r^{-6} potential at crystallization, in the low k -region

$k\sigma$	Original†	Case I	Case II	Case III
0.2	0.0091	0.0098	0.0091	0.0098
0.6	0.0096	0.0101	0.0096	0.0101
1.0	0.0104	0.0106	0.0104	0.0106
1.4	0.0117	0.0118	0.0117	0.0118
1.8	0.0136	0.0136	0.0135	0.0135
2.2	0.0163	0.0163	0.0158	0.0158
2.6	0.0200	0.0200	0.0192	0.0192
3.0	0.0251	0.0251	0.0247	0.0247
3.4	0.0324	0.0324	0.0324	0.0324
3.8	0.0432	0.0432	0.0432	0.0432

† From Table IV of Hansen and Schiff.⁸

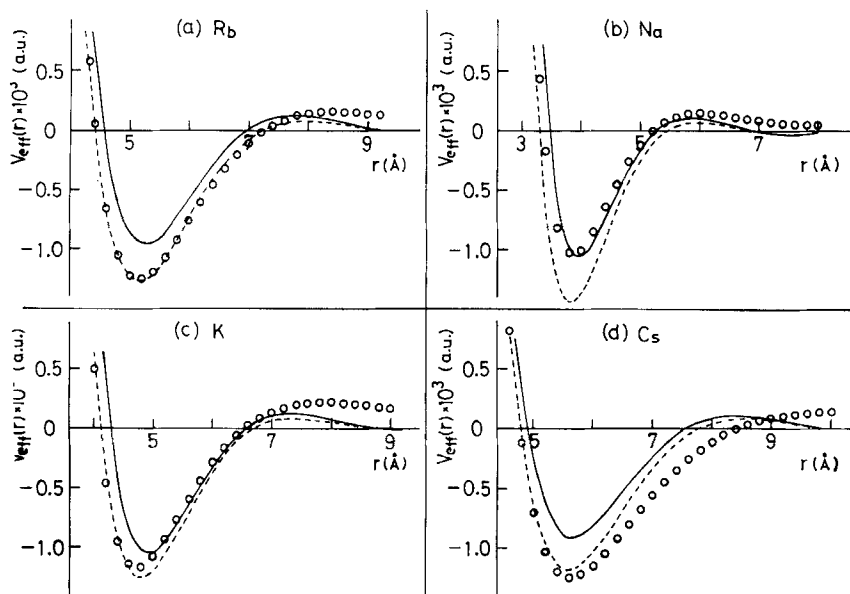


FIGURE 9 Comparison of the effective pair-potentials, based on the modified MC $a(k)$ labelled case III in Table 1, with those obtained via pseudopotential theories. (a): liquid Rb at 319K, (b): liquid Na at 373K, (c): liquid K at 338K and (d): liquid Cs at 303K; solid line: from Bratkovsky *et al.*, broken line: from Price *et al.*

Price *et al.*, while the attractive part is quite similar to that of Bratkovsky *et al.* with an exaggerated hump at larger r . In the case of liquid Cs the result is similar in shape to that of Price *et al.*, though giving an appreciably suppressed attractive part. In any case the exaggerated hump in the attractive part at larger r is a common feature to all cases studied, which is probably attributable to the inadequacies in case III. Nevertheless, the present results appear to be compatible with those obtained from the pseudopotential theories. There have been a variety of effective pair-potentials obtained from observed structure factor data via various approximate methods but we have not quoted here any of them for the purpose of avoiding complexity.

III CONCLUSIONS

Using the RPA and the MC simulation data we have investigated the $v_{\text{eff}}(r)$ in liquid alkali metals, and discussed on the sensitivity of the latter to probable errors in the MC $a(k)$. In spite of this uncertainty in the low angle region we believe that the present approach can offer reliable information about the

$v_{\text{eff}}(r)$, even though it may not be feasible to obtain a unique $v_{\text{eff}}(r)$. We can regard the result for Rb as a demonstration of the usefulness of the present method. So, though the RPA method is often said to be semiquantitative, it works very well if an accurate reference system is used in describing $v_{\text{core}}(r)$.

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