The role of the pair potential in determining the structure factor of liquid rubidium

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Abstract. The role of the pair potential in determining the behaviour of density and wavenumber derivatives of the structure factor of liquid rubidium is assessed. By solving the Percus–Yevick approximation numerically for the Price effective interionic potential and related potentials, the effects of various parts of the interionic interaction can be delineated. The conclusion of this study is that the agreement between the structure factor derivatives and the high accuracy of the Price potential results are the result of the combined effect of the softness of the repulsion and the non-monotonic nature of the tail of the potential.

1. Introduction

Recently, considerable interest has focused on the relationship between wavenumber \( q \) and density \( \rho \) derivatives of the structure factor \( S(q) \) for liquid metals. This interest was prompted by the experimental results of Egelstaff and co-workers (Egelstaff et al 1971, 1980) in which the structure factor of liquid rubidium was measured on a grid of temperature–density points in the phase plane such that density derivatives of \( S(q) \) were obtained. They interpreted these results in terms of the uniform-fluid model (UFM) (Egelstaff et al 1971). The UFM can be characterised as follows: for a liquid-metal effective interionic pair potential \( \varphi(r) \) derived from pseudopotential theory, it is known that at large separations \( \varphi(r) \) takes on the asymptotic form

\[
\varphi(r) \sim \cos 2k_F r/r^3 \quad \text{as } r \to \infty.
\]

We assume that the density dependence of the Fermi wavenumber—\( k_F \sim \rho^{1/3} \)—induces a characteristic scaling of \( r \), so \( r \sim \rho^{-1/3} \). Hence, the radial distribution function \( g(r) \), proportional to the probability density of finding a metal ion a distance \( r \) away from another metal ion, is a universal function \( \hat{g}(x) \) where \( x = r \rho^{1/3} \) and \( S(q) \) is a universal function \( \hat{S}(y) \) where \( y = q \rho^{-1/3} \). This leads to the prediction

\[
\rho \partial S(q)/\partial \rho \approx -q \partial \hat{S}(q)/\partial q.
\]

The UFM was verified experimentally for liquid Rb in the vicinity of the first peak of \( S(q) \) (Egelstaff et al 1971, 1980), the expected region of validity of the UFM. Egelstaff and Wang (1972) have also shown that the UFM does not agree with data on neon or the Lennard–Jones fluid. In a solid, the geometrical arrangement of the molecules generally does not change with density and the intermolecular separations vary as \( \rho^{-1/3} \). In this case, the scaling property of \( g(r) \) assumed in the UFM can be expected to be virtually exact. One
consequence of the unchanging geometric arrangement is that the number of nearest neighbours does not vary with density. Thus, constancy of the number of nearest neighbours at constant temperature can be regarded as one of the assumptions implicit in the derivation of the UFM for liquid metals. Since the nearest-neighbour packing changes for simple fluids with increasing density, this is likely to be one of the primary reasons for the failure of the UFM for such systems.

Recently, Cummings and Egelstaff (1982) focused attention on the assumptions of the UFM and attempted to determine whether the success of the UFM could be attributed to the simple scaling argument given in its derivation outlined above or whether its origin lay instead (or in part) in other features of the effective interionic potential. In particular, Cummings and Egelstaff addressed directly the two following questions: how important is the density dependence of the pair potential in yielding UFM behaviour and how important is the oscillatory tail. These issues represent two of the three major differences between simple-fluid pair potentials (which are monotonic at large beyond the repulsive-force region and independent of the density.). The third major difference between simple-fluid pair potentials and liquid-metal effective interionic potentials is the relative harshness of the repulsion in the former (effectively modelled as $1/r^{12}$) compared with that on the latter (effectively modelled as $1/r^{4}$). The method employed by Cummings and Egelstaff (1982) consisted of solving the mean-spherical approximation (MSA) (Lebowitz and Percus 1966), for three model fluids: the hard-sphere fluid, the Yukawa fluid (a model for simple fluids such as argon whose molecules have a hard core and attractive, monotonic, exponentially decaying attraction) and a model liquid metal (whose ions have hard cores and interact via an oscillatory, exponentially decaying). Specifically, the pair potentials for these three systems are given by

\[
\phi_{\text{HS}}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \quad \text{(3)}
\]

\[
\phi_{\text{Y}}(r) = \begin{cases} \infty & r < \sigma \\ -(J/r) \exp[-z(r-\sigma)] & r > \sigma \end{cases} \quad \text{(4)}
\]

\[
\phi_{\text{MLM}}(r) = \begin{cases} \infty & r < \sigma \\ -(D/r) \exp[-z(r-\sigma)] \cos(2k_F r + \delta) & r > \sigma \end{cases} \quad \text{(5)}
\]

where the subscripts HS, Y and MLM denote hard sphere, Yukawa and model liquid-metal potentials respectively, $\sigma$ is the hard-core diameter in each case and $J$, $D$ and $\delta$ are constants characterising the strength, decay and phase of the tail parts of the potentials. The MSA is defined in terms of the radial distribution function $g(r)$ (which, in the case of liquid metals, is proportional to the probability density of finding an ion at distance $r$ from a given ion) and the direct correlation function $c(r)$ which is defined by the Ornstein–Zernike equation (Ornstein and Zernike 1914)

\[
h(r) = c(r) + \rho \int c(|s|) h(|r-s|) \, ds. \quad \text{(6)}
\]

In equation (6), the total correlation function $h(r)$ is defined to be the deviation of $g(r)$ from its ideal-gas value of 1 (i.e., $h(r) = g(r) - 1$). The MSA for hard-core systems is then given by the exact core condition

\[
g(r) = 0 \quad (\equiv h(r) = -1) \quad r < \sigma \quad \text{(7a)}
\]

combined with the approximation

\[
c(r) = -\phi(r)/k_B T \quad r > \sigma \quad \text{(7b)}
\]
where $k_B$ is Boltzmann's constant and $T$ is the absolute temperature. Equation (7b) represents the extrapolation of the large-separation asymptotic behaviour of $c(r)$ to short ranges.

The advantage of studying three models given in equations (3) to (5) is threefold: the MSA is analytically solvable for all three models (Wertheim 1963, Thiele 1963, Waisman 1973, Cummings and Smith 1978a, b, Cummings 1979) thus making the calculation of the structural properties rapid and routine; the use of the same integral equation approximation for each Hamiltonian might conceivably eliminate much of the error in such approximations by focusing on the difference between the results for the three systems rather than concentrating on the values of the structural properties themselves; each of the pair potentials differed in specific ways which bore directly on the two issues foremost in the study. The reader is referred to the original paper (Cummings and Egelstaff 1982) for the specific results; however, the conclusions of the study can be summarised as follows: as might be expected on the basis of the experimental results, neither the hard-sphere nor the Yukawa fluid exhibited UFM-like behaviour except at densities normally associated with the solid state while the model liquid metal did exhibit UFM-like agreement between the derivatives of the structure factor; the density dependence of the pair potential appears to make some contribution to the UFM-like behaviour observed in the model liquid-metal system; that UFM-like behaviour is observed in the model liquid-metal system suggests that the oscillatory tail of the potential plays a significant role in contributing toward UFM behaviour. Cummings and Egelstaff (1982) did not assess the role of core softness in their study, noting that an attempt to do so using the soft-core model of Hoshino (1980) led to physically unacceptable density derivatives of the structure factor. Thus, on the basis of their analysis, Cummings and Egelstaff reached two conclusions: first, the prime feature of liquid-metal potentials that causes UFM behaviour is the oscillatory nature of the potential; second, the density dependence of the potential made a lesser but nevertheless significant contribution towards UFM behaviour. (It should be noted that the conclusions of Cummings and Egelstaff were based on comparing fluids with hard cores and the validity of their results is dependent on the extent to which this is a good approximation for real liquid metals.)

The conclusions of Cummings and Egelstaff were disputed by Hayter et al. (1983) who suggest that the softness of the repulsive core is the major determining factor in liquid metals exhibiting UFM behaviour. Their conclusions were based on results obtained from the solution of the MSA for the repulsive Yukawa fluid, a fluid having a hard core and rapidly exponentially decaying repulsion thus yielding a fluid with a soft core. Specifically, the model interionic potential employed by Hayter and co-workers is given by

$$\varphi_H(r) = \begin{cases} \infty & r < \sigma \\ \left(\frac{J}{r}\right) \exp\left[-z(r-\sigma)\right] & r > \sigma \end{cases}$$

(8)

From their results they conclude that the soft core is the determining factor that yields UFM-like behaviour. They also obtained structure factors for Na, K and Rb using $\varphi_H(r)$, which were in agreement with existing experimental data. However, the results were obtained by back-fitting the three parameters, $J$, $z$ and $\sigma$, to the experimental structure factor. The resulting Yukawa fluid is steeply repulsive (i.e., $z\sigma = 8.9$) and has a large value at contact ($\varphi_H(r)/k_B T = 7.23$ at $r = \sigma$). Recently, Tau and Reatto (1985) have questioned the accuracy of the MSA for fluids interacting via steeply attractive Yukawa potentials with large values at contact. Tau and Reatto base their conclusions on the inconsistency between the various routes to the thermodynamic properties. The underlying cause of the inaccuracy of the MSA for such potentials must be related to the failure of one of the key
assumptions of the MSA which is that the pair potential is small enough that
\[ \exp\left(-\frac{\varphi(r)}{k_B T}\right) - 1 \simeq -\frac{\varphi(r)}{k_B T}. \]
This suggests that the MSA may not be very reliable for steeply repulsive Yukawa potentials (although it must be remarked that this has not been established quantitatively).

At this juncture, then, it appears that the question of which features of the liquid-metal interionic potential are most important for agreement with the UFM is still not completely resolved. In this paper, we attempt to address this issue more directly than did either of the previous two studies reviewed above through an examination of the structural properties of liquid rubidium as obtained from a realistic model for the interionic potential. We report numerical solution of the Percus–Yevick (PY) approximation (Percus and Yevick 1958) for the Price potential of liquid rubidium (Price et al 1970, Price 1971) and calculate the derivatives of the structure factor \( S(q) \) with respect to \( q \) and \( \rho \). These derivatives are compared with experimental results for liquid Rb and with the Lennard-Jones fluid for the "same" reduced-state conditions. The PY approximation is given by the OZ equation (6) subject to the approximate closure
\[ c(r) = \frac{\exp\left(-\frac{\varphi(r)}{k_B T}\right) - 1}{g(r) - c(r)}. \]

The PY approximation is chosen because its strengths and its limitations are well known and documented in liquid-state physics. In the most comprehensive study of the PY approximation and two other integral equation approximations (the hypernetted chain and Born–Green–Yvon–Kirkwood approximations reviewed by Hansen and McDonald 1976) published to date, Levesque found that for the Lennard-Jones and square-well fluids the PY approximation was the best of these approximations over a wide range of density and pressure (Levesque 1966). On this basis, we can expect the PY approximation to be at least qualitatively reliable for liquid-metal systems and, perhaps, quantitatively so.

Our method is described in § 2. As described in § 3, the PY approximation with the Price potential gives excellent agreement with experimental structure factor derivatives. Also in § 3, we discuss the features of the liquid-metal potential which lead to agreement with experiment. We conclude that it is a combination of the oscillatory tail and soft repulsion of the potential that is responsible for the UFM-like behaviour and the agreement with experiment. This validates the conclusions of both Cummings and Egelstaff (1982) on the importance of the tail of the interionic potential and Hayter et al (1983) on the importance of the softness of the repulsion. We must emphasise that, unlike in the latter of these two studies, there are no adjustable constants used in the pair potential to optimise agreement with experiment. More precisely, the results presented are obtained from the PY approximation applied to the Price potential as prescribed by Price and co-workers (Price et al 1970, Price 1971); the Price potential was not modified in any way in order to optimise agreement between our results and the experimental results of Egelstaff and co-workers.

2. Method

Numerical calculations of liquid Rb structure factors were performed using a program written by Monson (1982) (based on Gillan's method for solving the Percus–Yevick equation numerically (Gillan 1979), and adapted for our purposes). The Price potential has been shown to yield accurate structural properties for liquid Rb near the triple point (i.e. \( T=318 \text{ K} \) and \( \rho=0.01057 \text{ Å}^{-3} \)) (Copeley and Rowe...
Figure 1. A comparison of potentials used in this study. In (a), the Price potential (full curve) for liquid rubidium at number density \( \rho = 0.01047 \text{ Å}^{-3} \) is compared with the Lennard-Jones potential (broken curve) with \( \sigma = 4.4 \text{ Å} \) and minimum energy \( \epsilon/k_B = 399 \text{ K} \). It is evident that the Lennard-Jones potential has the same minimum energy as the Price potential and has its zero located at a similar value of separation. In (b), the truncated Price potential (full curve) for liquid rubidium at number density \( \rho = 0.01047 \text{ Å}^{-3} \) is compared with the truncated Lennard-Jones potential (broken curve) and the repulsive Yukawa potential of Hayter et al (1983) (chain curve). See equation (13) for the definition used for the truncated potentials.

1974, Rahman 1974). At higher temperatures (600–1400 K) and lower densities (0.00963–0.00692 Å\(^{-3}\)), Mountain (1978) concluded on the basis of Monte Carlo simulations of the structure factor that the Price potential is less accurate quantitatively. The potential, as with all ion–ion effective potentials calculated on the basis of pseudopotential theory, is dependent on the density. The density dependence, while evident in most major features of the potential, is explicit in a formal mathematical sense through the asymptotic form given in (1), since \( k_F \sim \rho^{1/3} \). The density dependence of the major features of the Price potential was discussed by Cummings and Egelstaff (1982); one of
their conclusions is that the location of the first zero of the Price potential (i.e., the leftmost one when viewing figure 1(a)) is relatively independent of density.

In order to calculate the density and wavenumber derivatives of the structure factor, the Price potential was calculated at densities $\rho - \Delta \rho$, $\rho$ and $\rho + \Delta \rho$ (where $\rho = 0.01047 \text{ Å}^{-3}$ and $\Delta \rho = 6 \times 10^{-5} \text{ Å}^{-3}$) and the Percus–Yevick equation was solved to give structure factors $S(\rho - \Delta \rho; q)$, $S(\rho; q)$ and $S(\rho + \Delta \rho; q)$ respectively. The derivatives in equation (2) were then obtained from

$$\frac{\partial S(q)}{\partial \rho} = \rho \frac{S(\rho + \Delta \rho; q) - S(\rho - \Delta \rho; q)}{2\Delta \rho}$$ 

and

$$-\frac{1}{q} \frac{\partial S(q)}{\partial q} = -\frac{1}{q} \frac{S(\rho; q + \Delta q/2) - S(\rho; q - \Delta q/2)}{\Delta q}.$$ 

The Price potential at this density ($\rho = 0.01047 \text{ Å}^{-3}$) is shown in figure 1(a). For comparison, the Lennard-Jones (LJ) potential $\varphi_{\text{LJ}}(r)$ with much the same zero point ($\sigma = 4.4 \text{ Å}$) and well depth ($e/k_B = 399 \text{ K}$) is also shown. It is clear that the LJ potential, given by

$$\varphi_{\text{LJ}}(r) = 4e[(\sigma/r)^{12} - (\sigma/r)^6]$$

is more steeply repulsive than the Price potential. This is indicated by the slope of the former being steeper for $r < \sigma$. This figure also illustrates the difference between the LJ and Price potentials for separations greater than at the minimum-energy point.

3. Results and conclusions

Figure 2(a) shows the derivatives of the structure factor obtained using the full Price potential calculated at density $\rho = 0.01047 \text{ Å}^{-3}$ and temperature 328 K. This state point is very close to the triple point, so in view of the comments in the previous section, the Price potential can be regarded as reliable here. The agreement between the theoretical results and the experimental data of Egelstaff et al. (1980) is very good. To some extent, one might argue that this good agreement is the result of a fortuitous cancellation in errors in the Price potential and in the PY approximation. Only a series of computer simulation studies yielding $S(q)$ and its derivatives could unequivocally assess the role of the two approximations. Unfortunately, as Mountain (1978) points out, calculating $S(q)$ from simulation yields limited results (due to periodic boundary conditions) with significant noise levels (in typical length simulations) suggesting that the derivatives of $S(q)$ would contain substantial errors. In the absence of such simulation data, one can only infer that, on the basis of the known accuracy of the Price potential for the structural properties of Rb at these state conditions (Copeley and Rowe 1974, Rahman 1974) and our agreement with the experimental results, the error in the PY approximation must be quite low. We therefore conclude that although we cannot rule out the possibility that the agreement with experiment shown in figure 2(a) is the result of a fortuitous cancellation of errors the available evidence suggests that this is not the case.

In addition to the agreement between theory and experiment shown in figure 2(a), we note that both the theoretical and experimental derivatives of the structure factor exhibit the expected UFM property of agreement between density and wavenumber derivatives. For
Figure 2. The density (full curves) and wavenumber (broken curves) derivatives of the structure factor \((\partial \bar{S} / \partial q, -(q/3) \partial \bar{S} / \partial q)\) respectively) obtained from solution of the Percus-Yevick approximation. In (a) the theoretical results are obtained using the Percus-Yevick approximation applied to the Price potential which exhibits full density dependence and are compared with the corresponding experimental results (full and open circles respectively) for liquid rubidium at \(\rho = 0.01047 \text{ Å}^{-3}\) and temperature \(T = 328 \text{ K}\). In (b), the results are shown for the Lennard-Jones fluid at the same density and temperature.

comparison with a simple fluid at the same temperature and density, the structure factor derivatives were obtained using the Lennard-Jones potential of figure 1(a) and are shown in
Two important conclusions from these results. First, the excellent agreement between the predictions of the PY approximation applied to the Price potential and the experimental results suggest that the Price potential has one or more essential characteristics required of a pair potential in order for it to satisfy the UFM. In addition to satisfying the UFM in the qualitative sense, the Price potential yields quantitatively correct estimates of the structure factor derivatives. By the same reasoning, the failure of the LJ potential to comply with the UFM at the same reduced-state conditions implies that in the differences between the Price and LJ potentials lies the explanation for the applicability of the UFM to liquid metals and its inapplicability to simple fluids such as argon.

There are three major qualitative differences between the LJ and Price potentials, two of which are revealed by inspection of figure 1(a): the repulsive part of the LJ potential is considerably harsher than that of the Price potential; the LJ potential is monotonic beyond its minimum while the Price potential is oscillatory. Additionally, as noted in §1, the Price potential is dependent on density while the LJ potential is independent of density. We now investigate the relative importance of these three factors in determining UFM behaviour and the quantitative agreement with experiment. We adopt the same strategy as Cummings and Egelstaff (1982); that is, we examine the structure factor derivatives for liquid metals and simple fluids using the same integral equation approximation (PY) for each system with the hope that differences between results for the various pair potentials are free of any systematic errors in the approximations themselves. As will be evident, this leads to one conclusion (that density dependence in the pair potential is unimportant in yielding UFM behaviour) which is at variance with the corresponding conclusion of Cummings and Egelstaff (1982). We contend that this is due to the difference between the pair potential models used (hard-core potentials used by Cummings and Egelstaff, realistic potentials with soft cores used in the present work) and is not due to the different approximations used (MSA by Cummings and Egelstaff, PY in this paper).

To probe the importance of the density dependence of the Price potential, structure factor derivatives were calculated with the Price potential forced to be independent of the density—i.e., $\varphi(p - \Delta p; r) = \varphi(p + \Delta p; r) = \varphi(p; r)$. On the scale of figures 2(a) and 2(b), it was found that the structure factor derivatives for the density-independent Price potential were indistinguishable from those for the fully density-dependent potential, implying that the shape of the potential is much more important than its density dependence in determining the structural properties of liquid rubidium. For the most part, this conclusion is consistent with the findings of Cummings and Egelstaff (1982), although Cummings and Egelstaff incorrectly assigned a greater role to the density dependence than is evidently justified by the present results.

In order to investigate the role of repulsion alone, structure factor derivatives were obtained for truncated Price and Lennard-Jones potentials. The truncated potentials are obtained using the Weeks-Chandler-Anderson prescription (Anderson et al 1976) which defines the truncated potential $\varphi_T(r)$ by

$$
\varphi_T(r) = \begin{cases} 
\varphi(r) + \varphi(r_{\text{min}}) & r < r_{\text{min}} \\
0 & r > r_{\text{min}} 
\end{cases}
$$

where $r_{\text{min}}$ is the separation corresponding to the minimum of the potential. Thus, the truncated potential is defined as the continuous purely repulsive potential exerting the same repulsive force as the original potential. The truncated Price and LJ potentials are shown in figure 1(b) and the results for structure factor derivatives are shown in figure 3. The
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Figure 3. The density (full curves) and wavenumber (broken curves) derivatives of the structure factor \( \rho \partial S / \partial q \) and \(- (q/3) \partial S / \partial q\) respectively) at \( \rho = 0.01047 \, \text{Å}^{-3} \) and temperature \( T = 328 \, \text{K} \) as predicted by the Percus–Yevick approximation. In (a), the truncated Price potential shown in figure 1(b) was used for the interionic potential while in (b) the truncated Lennard-Jones potential was used.

The truncated Price potential gives UFM-type agreement while the truncated LJ potential does not. However, the amplitudes of the derivatives for the truncated Price potential are higher than those obtained for the full Price potential. Hence, the structure factor derivatives for the truncated Price potential do not agree with the experimental data. These results indicate that short-range softness of the potential is clearly an important factor in obtaining qualitative UFM behaviour, but to obtain agreement with experimental data the oscillatory tail must be included. (These results show that the effect of the oscillatory tail is to reduce the magnitude of the structure factor and its derivatives. Evidently, the difference between the actual behaviour reported in this paper and that conjectured by Cummings and Egelstaff is due to the quite different structural effects of soft- and hard-core repulsion.)

We note that since UFM behaviour is obtainable from solely a soft repulsive interaction, this agrees in part with the conclusions of Hayter et al. (1983), referred to as HPS. However, we see that in the absence of the oscillatory tail of the Price potential the computed derivatives do not agree in magnitude with the experimental results. It appears likely, however, that a suitably chosen repulsive interaction could be developed whose structure factor derivatives agree with the experimental results. This would be done by adjusting the harshness and magnitude of the interaction, as did HPS. From the results presented here, it is clear that a purely repulsive interaction able to yield agreement with the experimental data would differ considerably from the Price potential, and this is shown in figure 1(b) where we compare the repulsive part of the Price potential with that of HPS. The most striking difference between the truncated Price potential and the HPS potential is the considerably larger core of the latter. This suggests that the effective (reduced) density of a fluid interacting via the HPS potential will be considerably higher than that of a fluid interacting via the repulsive Price potential (which in turn is higher than that of a fluid interacting with the full Price potential). As noted in § 1, UFM-like behaviour can be
obtained from the hard-sphere and attractive Yukawa fluids in the MSA at sufficiently high reduced density; it is feasible, then, that the UFM behaviour observed using the HPS potential in the MSA is due—at least in part—to the high reduced densities involved in this case.

From inspection of the two potentials in figure 1(a), one might suppose that perhaps the key difference between the LJ and Price potentials is the fact that the Price potential has a well defined bowl between the first (at 4.4 Å) and second (at 7.15 Å) zeros of the potential while the LJ potential does not. This is suggested by our reluctance to attribute a significant role to those parts of the potential whose magnitude is small compared with the attraction. Structure factor derivatives were calculated using the Price potential set to zero beyond 7.15 Å. This potential yielded behaviour intermediate between that of the purely repulsive Price potential and the full Price potential, implying that the features beyond 7.15 Å have a discernible effect on the results for the structure factor derivatives.

The conclusions one may draw from the results reported in this paper are that both the softness of the repulsion and the non-monotonic nature of the tail of the potential are responsible for UFM behaviour which agrees quantitatively with experimental data, and that density effects in the interionic potential are relatively unimportant.

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