

A NEW PERTURBATION THEORY FOR POTENTIALS
WITH A SOFT CORE. II. APPLICATION
TO LIQUID SODIUM

by

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ABSTRACT

An extension of the Weeks-Chandler-Andersen perturbation theory, proposed by Wright and Perram [Chem. Phys. Letts. 66 (1979) 274] is applied to liquid Na. By neglecting the potential beyond its first minimum, the structure factor is found to be given accurately except in the vicinity of the first peak.

I. INTRODUCTION

The physical properties of the liquid alkali metals have allowed detailed study of their structural and thermodynamic properties through the formalism of the theory of simple liquids (for an early review see March [1]). The near spherical Fermi surface of the conduction electrons allows the ions to be thought of as embedded in a uniform neutralising background. Thus the ions are considered to be a simple liquid interacting via a volume dependent interionic potential that is repulsive at small separations and oscillatory at large separations.

The form of the potential $\phi(r)$ as predicted by pseudopotential theory (Harrison [2]) may be written

$$\phi(r) = \phi_{\text{REP}}(r) + \phi_{\text{LRO}}(r) \quad (1)$$

where $\phi_{\text{REP}}(r)$ refers to the repulsive part which dominates at small r and $\phi_{\text{LRO}}(r)$ refers to the long range oscillations which dominate at large r . The asymptotic form of $\phi_{\text{LRO}}(r)$ is given by

$$\phi_{\text{LRO}}(r) \sim \frac{A \cos(2k_{\text{F}}r + \delta)}{r^3} \quad (2)$$

where A and δ are constants, k_{F} is the Fermi wavenumber [$k_{\text{F}} = (3\pi^2 \rho Z)^{1/3}$ where ρ is the number density of ions and Z is the valence].

As for the repulsive part there is growing consensus [3,4] that for alkali metals $\phi_{\text{REP}}(r)$ is softer than it is for polyvalent metals and the rare gases. The latter are usually modelled by a two parameter

Lennard-Jones potential for which $\phi_{\text{REP}}(r) \sim 1/r^{12}$ small r . However, Hansen and Schiff [5,6] on the basis of static structural properties suggest that a more appropriate form for liquid sodium is

$$\phi_{\text{REP}}(r) \sim 1/r^4 \quad \text{small } r$$

In the case of Rubidium this degree of softness is also present as shown in the elegant work of Rahman [7] and Mountain, *et al.* [4,8]. Their molecular dynamics simulations using the Price potential [9] indicate that liquid Rb supports sound modes of wavelengths as low as 1.25 times the equilibrium separation of the ions, in good agreement with the experimental results [10]. In contrast the molecular dynamic results of Levesque [11] show that the Lennard-Jones fluid supports sound modes of wavelength no smaller than 5 times the equilibrium separation, in good agreement with experiments on the rare gases [12]. Mountain, *et al.* [4,8] trace this difference in dynamic properties to differences in the repulsive parts of the pair potentials.

This observation is important in that it is now relatively well established that at high density much of the liquid structure is determined by repulsive forces between the particles. This assumption underlies the Weeks, Chandler, Andersen (WCA) perturbation theory [13,14], which is successful in predicting high density structure for harshly repulsive potentials. In this paper we examine the applicability of the WCA theory to a liquid alkali metal (i.e., Na) for which $\phi_{\text{REP}}(r)$ is quite soft.

In Section II we give the salient equations of the perturbation theory adopted by us within the context of the parametric reference system introduced in an earlier paper by Perram and Wright [15] (hereafter referred to as I). In Section III we conclude with a discussion of our results for liquid Na at 100°C for the liquid sodium potential used by Murphy and Klein in their accurate simulation study [16].

II. COMPUTATIONAL METHOD

In this section we describe the method used to calculate the structure factor for a fluid system in which the pair potential is purely repulsive. Specifically we are interested in the repulsive force part of the liquid sodium potential from zero separation to its first minimum at $r = R_m = 3.824 \text{ \AA}$. We adopt the WCA theory [13,14] which begins by writing the potential as

$$\phi(r) = u(r) + w(r) \quad (3a)$$

where

$$\begin{aligned} u(r) &= \phi(r) - \phi(R_m) & r < R_m \\ &= 0 & r > R_m \end{aligned} \quad (3b)$$

The essential point of the WCA theory is that at high densities, all the structural properties of a fluid interacting via the potential (3a) are, to a good quantitative approximation, given by the corresponding properties for a fluid interacting via the potential (3b)

alone. The next step in the WCA theory is to relate the structural properties of a fluid interacting via the truncated potential $u(r)$ to those of a reference system. (See ref. [13] for a detailed review.) The subscript "0" is used for reference system quantities.

A functional Taylor's expansion for the correlation function $y(r) = g(r)\exp(\beta u(r))$ [where $g(r)$ is the radial distribution function, $\beta = 1/kT$ where k is Boltzmann's constant and T is absolute temperature] in terms of the Boltzmann factor yields

$$y(r) = y_0(r) + O(\xi^2) \quad (4)$$

The corresponding expression for the structure factor $\hat{S}(k)$ is given by

$$\hat{S}(k) = \hat{S}_0(k) + \rho \hat{B}(k) \quad (5)$$

where $\hat{B}(k)$ is the Fourier transform of $B(r)$, the "blip function", given by

$$B(r) = y_0(r) [e^{-\beta u(r)} - e^{-\beta u_0(r)}] \quad (6)$$

where $u_0(r)$ is the pair potential for the reference system.

The error parameter ξ is defined by

$$\xi = \int |B(r)| d\vec{r}$$

where the integral is over all space.

When implementing Eq. (4) the reference system is to be chosen so that

$$\hat{B}(0) = 0 \quad (7)$$

The usual reference system used is a hard sphere system with effective diameter chosen by Eq. (7). For harshly repulsive potentials this is satisfactory in that the error parameter ξ which is a measure of the non-zero width of $B(r)$ is small. However, for softer potentials the deviation from hard sphere is too drastic and higher order terms for $y(r)$ containing 3 and 4 body distributions need to be considered. For example Kumaravadivel and Evans [3] found that the WCA procedure gave good results for polyvalent metals but was poor for the softer liquid alkali metals.

To overcome this problem and yet retain the simplicity of the WCA theory we propose to use the parametric reference system introduced by Perram and Wright in I. We assume that the reference system total correlation function [$h(r) = g(r) - 1$] may be written

$$h_{sc}(r) = -1 + \frac{\alpha \lambda^2}{\cosh \lambda R} \left(\frac{\sinh \lambda r}{\lambda r} - 1 \right) \quad r < R \quad (9)$$

where α , λ are parameters to be determined. We use the subscript "sc" to indicate quantities in our "soft core" reference system. The value of R provides another condition on the reference system in that the direct correlation function $c_{sc}(r)$, defined by the Ornstein-Zernike equation, satisfies

$$c_{sc}(r) = 0 \quad r > R \quad (10)$$

The reference system potential to be used in Eqs. (6) and (7) is then taken to be the Percus-Yevick (PY) potential

$$u_{PY}(r) = \log[1 - c_{sc}(r)/g_{sc}(r)] \quad (11)$$

where $c_{sc}(r)$ on $0 < r < R$ is given by (see I for details)

$$rc_{sc}(r) = -q'(r) + 2\pi\rho \int_0^{R-r} q(t)q'(t+r)dt \quad (13a)$$

where

$$q(r) = q_1(x-R) + \frac{1}{2} q_2(r^2 - R^2) + q_3(\sinh\lambda r - \sinh\lambda R) \\ + q_4(\cosh\lambda r - \cosh\lambda R) \quad (13b)$$

The parameters q_i , $i = 1, \dots, 4$, are the solutions of a set of simultaneous linear equations.

A further modification of the WCA theory that we use when calculating the structure factor is due to Jacobs and Andersen (JA) [17]. Considering a partial summation of the higher order terms in $g(r)$ they suggest that a better approximation to $\hat{S}(k)$ than Eq. (4), provided $\hat{B}(k)$ is small is

$$\hat{S}(k) = \hat{S}_0(k) [1 + \rho\hat{B}(k)\hat{S}_0(k) + (\rho\hat{B}(k)\hat{S}_0(k))^2 + \dots] \\ = \hat{S}_0(k) / [1 - \rho\hat{B}(k)\hat{S}_0(k)] \quad (14)$$

This expression has the advantage of being less sensitive to the spurious behaviour of $\hat{B}(k)$ near $k = \pi/R$ as dictated by the blip function.

In their study JA postulated an interionic potential dependent on several parameters that could be adjusted to enable good fit of the experimental structure factor around its third peak. Having found the appropriate parameters they then use an effective hard

sphere reference system with diameter d chosen by Eq. (7) to calculate $\hat{S}(k)$ for their potential. They found Eq. (14) to be satisfactory from the second peak outwards for a wide range of soft potentials.

For our reference system the structure is known explicitly via

$$\hat{S}_{sc}(k) = 1/[\hat{Q}(k)]^2 \quad (15)$$

where

$$\hat{Q}(k) = 1 - 2\pi\rho \int_0^R e^{ikr} q(r)dr \quad (16)$$

and $q(r)$ is given by Eq. (13b).

Thus for any given set of α , λ and R all reference system quantities are known in closed form and may be evaluated readily.

III. RESULTS FOR LIQUID SODIUM

In this section we present the results for liquid Sodium at 100°C. The values of α , λ were obtained by

- i) requiring continuity of $h_{sc}(r)$ at $r = R$;
- ii) satisfying the "blip function" criterion, Eq. (7) with the relevant soft core functions replacing the "0" subscripted functions.

The first condition is satisfied if and only if (see I for details)

$$q'(R) = 0 \quad (17)$$

Eqs. (7) and (17) were satisfied by simple iteration on α and λ . The analyticity of $u_{PY}(r)$ and $y_{SC}(r)$ enable rapid evaluation of Eq. (7) at each step using any simple quadrature. We used Simpson's rule with 200 pts on $0 < r < R$.

Calculations were performed for three different values of R . The numerical values obtained are listed in Table I.

(Table I here)

In Figs. (1) - (3) we compare the structure factors calculated from Eqs. (15) and (16) using the data of Table I with the experimental results of Greenfeld, Wellendorf and Wiser [18] (GWW) for the full liquid sodium potential, and the WCA structure factor obtained using Eq. (5).

As expected the large k behaviour is adequately described by interionic repulsions. The best results were obtained when the full "repulsive force" portion of the potential is used ($R = 3.824 \text{ \AA}$). In Fig. 1 the experimental $\hat{S}(k)$ is reproduced from the second minimum onwards. The effect of the Friedel Oscillations is noticeable in the vicinity of the first two peaks which are shifted slightly to the left. A further point worth noting is that Eq. (17) should be at its worst for intermediate k values due to large oscillations in $\hat{B}(k)$. This is a possible source of error in the first two peaks. However the JA error parameter (see ref. [17]) E in this case is .23 which is inside the permissible limits estimated by Jacobs and Andersen and our $\hat{S}(k)$ should be a reasonable representation of the structure produced by the

repulsive potential in Eq. (3b). We note that the spurious behaviour of the WCA curve in the form of a dip at low k is not present in the JA curve. At larger k the two curves coincide as expected, both converging to $\hat{S}_{SC}(k)$. For decreasing R the structure when compared with experiment becomes increasingly worse (Figs. 2 and 3). Both the phase and amplitude are in error to quite a marked extent even though the values of the JA parameter E are small indicating that our $\hat{S}(k)$ is accurate for the repulsive part of the potential. This concurs with the observation that the Weeks, Chandler, Andersen split of the potential, using all the repulsive force part as the reference system, leads to a more rapidly convergent perturbation theory.

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TABLE I

Reference system parameters for the repulsive part of the liquid sodium potential [16] at 100°C. The large values of η reported should not be regarded as unphysical; they do not correspond to the usual definition of reduced density, since the scaling here is with respect to R , the position of the first peak in $g_{sc}(r)$.

R (Å)	$\eta = \frac{\pi}{6} \rho R^3$	α	λ	$E = \max[\rho \hat{B}(k)]$
3.824	0.7015	0.3013	7.29	0.23
3.5	0.538	0.2056	12.1	0.08
3.325	0.4613	0.138	19.4	0.02

FIGURE CAPTIONS

Figure 1. The structure factor for liquid Na at 100°C calculated using equation (14) with $R = 3.824$ Å. The crosses are taken from the experimental data of Greenfield, et al. [18]. The squares are the WCA pts, Eq. (5).

Figure 2. As for Fig. 1 with $R = 3.5$ Å.

Figure 3. As for Fig. 1 with $R = 3.325$ Å.

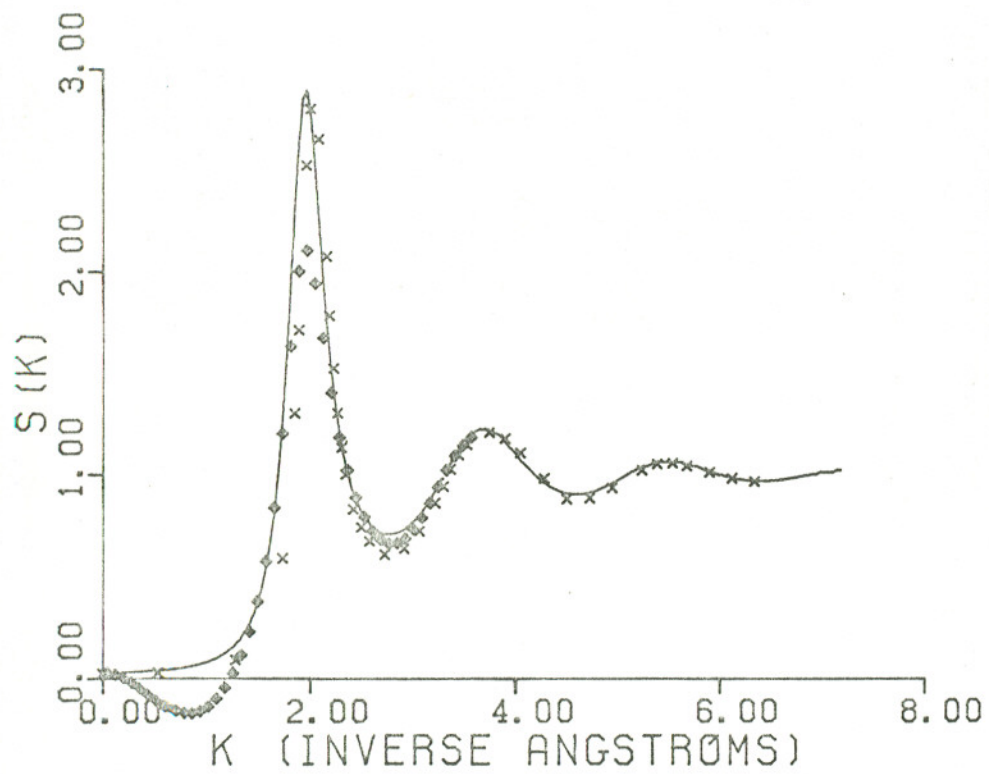


Figure 1

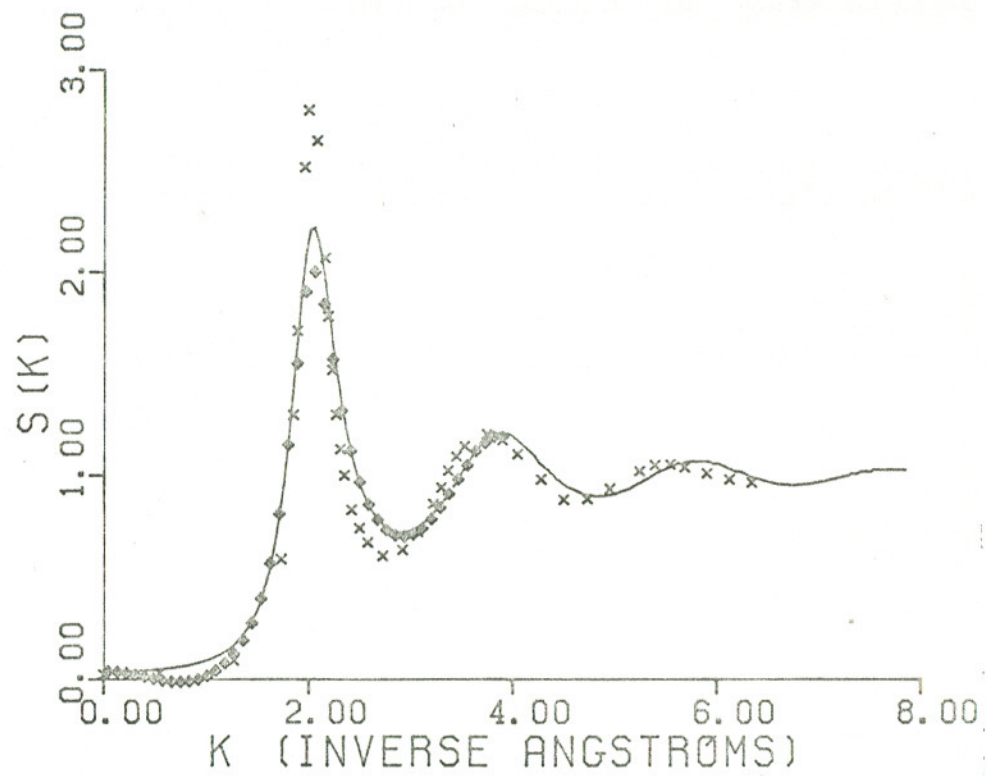


Figure 2

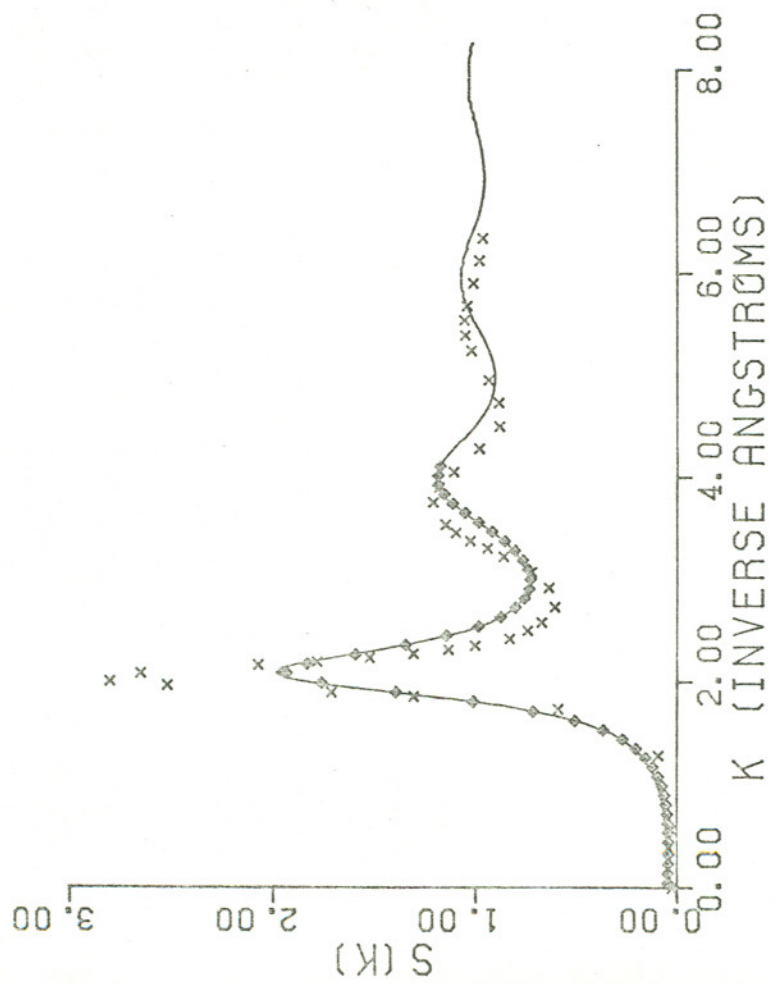


Figure 3