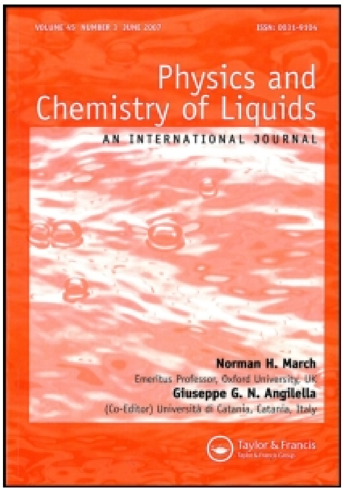

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M. A. Khaleque[a]; G. M. Bhuiyan[a]; R. I. M. A. Rashid[a]; S. M. M. Rahman[b]
[a] Department of Physics, University of Dhaka, Dhaka, Bangladesh [b] Department of Physics, College of Science, Sultan Qaboos University, Muscat, Sultanate of Oman

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CALCULATIONS OF S(q) FOR LIQUID 3d TRANSITION METALS

M. A. KHALEQUE, G. M. BHUIYAN, R. I. M. A. RASHID

Department of Physics, University of Dhaka, Dhaka: 1000, Bangladesh

S. M. M. RAHMAN

Department of Physics, College of Science, Sultan Qaboos University,
P.O. Box 36, Al-Khod, Postal Code: 123, Muscat, Sultanate of Oman

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Liquid structure for the 3d transition metals near melting is investigated using the linearized Weeks-Chandler-Andersen (LWCA) theory. Here the effective interionic pair potential is described by the Wills-Harrison model. Results show that LWCA predicts the structure factor much better than that of WCA. Results also show that in the middle of the 3d series LWCA predicts reasonable liquid structure where the WCA-ORPA has been unsuccessful.

KEY WORDS: Liquid transition metals, interionic pair potential, linearized Weeks-Chandler-Andersen theory.

1. INTRODUCTION

A substantial progress has been made over the last decade in our understanding of the structural and cohesive properties of less-simple and non-simple liquid metals[1–3]. The theories embrace both the refined perturbative treatments[4] and the first principles methods[5]. In this report we have presented results of calculations for the static structure factor $S(q)$, for liquid 3d transition metals. The linearized version[6] of the Weeks-Chandler-Andersen (WCA) theory of liquid structure has been applied. The Wills-Harrison model[7] is employed to treat the interatomic interactions; this model makes use of the separation between the free-electron-like and d-like states exhibited in transition-metal pseudopotential theory to treat the free-electron-like states with simple-metal theory.

The eminent task in calculating the liquid structure is to find a realistic expression for the pair distribution function $g(r)$, whose Fourier transform gives the structure factor $S(q)$. Finding an analytical expression for $g(r)$ for a **real** effective interconic potential experienced by an atom in a liquid is, however, a remote possibility[8]. Statistical mechanics for simple liquids indeed allows us to have an expression for the pair distribution function $g(r)$[9]. Consequently various approximate methods[6,10–12] have been developed to evaluate $g(r)$ and so $S(q)$.

The original form of the WCA approximation was extensively applied to calculate the liquid structure of simple metals[13-15]. Concurrently a linearised version of the WCA had been proposed by Meyer *et al*[6]. In the WCA method the pair correlation function $c(r)$ is defined as $c(r)=r^2B(r)$, where $B(r)$ is the so called "blip function" having the shape of two sharp teeth placed on the second and the fourth quadrant of the r-$c(r)$ plane (see ref. 10). The sides of the teeth away from the point of intersections are non-linear functions. Within the LWCA the nonlinear sides are approximated by straight lines and consequently the teeth-like-function transforms to a triangular function. When this is achieved one can expand $B(q)$, the Fourier transform of $B(r)$ about $r=\sigma$ (the hard sphere diameter), expressed in terms of a series (see ref. 6). Following the perturbation expansion of the Helmholtz free energy one can easily show that the free energy of the real system becomes equal to that of the reference system when the blip function vanishes[10]. Within the LWCA theory this condition leads to an equation having a transcendental from[6] amenable to numerical calculations; the solution of this equation gives the effective hard sphere diameter. It is known that the degree of accuracy of the LWCA method is comparable to the full method in the case of liquid simple metals.

Following the success of the LWCA in simple metals it is tempting to employ this method in 3d transition metals. It is also true that the presence of d-bands in the transition metals and in their liquids near melting makes a sharp distinction between the simple and transition metal properties[16]. However, the Wills-Harrison method of decomposing the effective pair potential into the *sp* and *d* components has initiated a move to combat this uncomfortable situation. The recent investigations of the structural properties of the transition metals using the WCA[17,18], WCA-ORPA[17,18], WCA-RPA[8], the integral equation theories[19,20] etc, reveal a partial success. In the light of this situation we are motivated to apply the LWCA in our present attempt aiming at a test of the concept of linearization that works very well in simple metals.

The calculated results of $S(q)$ for the 3d transition metals are compared to those evaluated by using different perturbation theories e.g. WCA, WCA-ORPA etc. in conjunction with the WH method. The present results exhibit some noticable successes over those of the WCA based calculations for most of the samples.

The layout of this paper is as follows in section 2 we briefly describe the WH model for effective pair interactions and the LWCA theory for liquids. We present and discuss our results in section 3 followed by some concluding remarks.

2. MATHEMATICAL FORMULATION

A. Effective Pair Potential:

From the transition metal pseudopotential theory the effective interionic pair potential may be written as[7]

$$V(r)=V_{\rm sp}(r)+V_{\rm drep}(r)+V_{\rm datt}(r) \tag{1}$$

where $V_{\mathrm{sp}}(r)$ represents the sp-band contribution to the effective pair potential and the other two terms represent the d-band contributions. Here V_{drep} arises from the shift of the d-band centre and V_{datt} is due to the contribution of the d-band energy. Explicitly (in atomic units),

$$V_{\mathrm{drep}}(r) = (225\, Z_d/\pi^2 (r_d^2/r^s) \tag{2}$$

and

$$V_{\mathrm{datt}}(r) = -(28.1\, Z_d/\pi)(1 - Z_d/10)(12/n)^{1/2}(r_d^3/r^5) \tag{3}$$

where n is the coordination number, r_d the atomic d-state radius and Z_d the effective number of d-electrons per atom. In our calculations we have used the values of r_d from WH[7] paper.

$V_{\mathrm{sp}}(r)$ in equation (1) has been treated by the simple metal theory where it can be expressed as[20]

$$V_{\mathrm{sp}}(r) = (Z_s^2/r)\{1 - 2/\pi \int_0^{\infty} F_N(q)[\sin(qr)/q]\,dq\} \tag{4}$$

where the normalized wave number characteristic is given by

$$F_N(q) = (q^2/4\pi\rho Z_s)v_0^2(q)[1 - 1/\epsilon(q)][1/(1 - G(q))] \tag{5}$$

In equations (4) and (5) Z_s represents the s-electron occupancy number, $v_0(q)$ the pseudopotential form factor, $\epsilon(q)$ the electronic dielectric function, $G(q)$ the local field correction and ρ the ionic number density. In this work we have followed WH[7] to describe $V_{\mathrm{sp}}(r)$, the sp-band contribution to the $V(r)$ which has been described by the empty core model. This model consists of two parameters: the core radius R_c and the effective s-electron number Z_s. Usually the values of R_c are determined by fitting the experimental data. It is known that the values of R_c obtained in this way from the pressure and bulk modulus show inconsistency[8]. Bhuiyan *et al*[20] and others[18,19] showed that when the values of R_c were suitably chosen in between the two fitted values of R_c good results for $S(q)$ could be obtained. We, in this calculation, have used the values of R_c from ref (20). Following the self consistent calculations by Moriarty[21] it has been shown[20] that when Z_s takes on values in the narrow range of $1.3 < Z_s < 1.7$ for the 3d transition metals at normal densities, results for $S(q)$ agree well with experimental data. For the sake of consistency we take the values of Z_s as well as R_c from the same work[20].

In this calculation Ichimaru-Utsumi[22] dielectric function has been used because it satisifes the self-consistency conditions in the compressibility sum rule and the short range correlation. Input data used in the calculations are listed in Table 1.

B. Weeks-Chandler-Andersen (Lwca) Approximation

The starting point for the LWCA method proposed by Meyer *et al*[6] is the WCA. In the WCA the blip function is defined[10] as

$$B(r) = Y_\sigma(r)\{\exp[-\beta u(r)] - \exp[-\beta u_\sigma(r)\} \tag{6}$$

Table 1 Input data used in the calculation. Here T is the temperature, ρ the ionic number density, Rc the core radius, Z_s the effective s-electron occupancy number and r_d the atomic d-shell radius.

Element	Z_s	$T(K)$	$\rho x 10^{-3}(au)$	$Rc(au)$	$r_d(au)$
Sc	1.7	1833	5.796	1.850	2.343
Ti	1.5	1973	7.731	1.840	2.041
V	1.4	2173	9.389	1.825	1.852
Cr	1.4	2173	10.761	1.615	1.701
Mn	1.4	1533	9.697	1.560	1.625
Fe	1.4	1833	11.201	1.425	1.512
Co	1.4	1823	11.659	1.235	1.436
Ni	1.5	1773	11.736	1.060	1.342

where $u(r)$ and $u_\sigma(r)$ are the soft sphere and hard sphere potentials respectively, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant and T is the temperature. In equation (6) $Y_\sigma(r)$ is the cavity function associated with the hard sphere distribution function. To evaluate $Y_\sigma(r)$ we follow Meyer *et al*[6]. The function $r^2 B(r)$, if plotted as a function of r, gives two sharp teeth shaped feature (for detail see ref[6]). In the LWCA it had been approximated by right angle triangles. Then the Fourier transform of $B(r)$ given by

$$B(q) = 4\pi \int_0^\infty B(r) r^2 \{\sin(qr)/qr\} dr \tag{7}$$

had been expanded in terms of the Bessel's function and the hard sphere pair distribution function to obtain a transcendental equation[6]

$$\beta u(\sigma) = \ln\{(-2\beta\sigma u'(\sigma) + Y + 2)/(-\beta\sigma u'(\sigma) + Y + 2)\} \tag{8}$$

The solution of (8) gives the correct value of hard sphere diameter σ. Usually in the WCA, σ is determined in such a way that

$$B(q = 0) = 0 \tag{9}$$

In equation (8) Y is given by

$$Y = (\sigma/\sigma_w g_o)\left[\sum(\xi_{n+1}(\eta_w)/n)(\sigma/\sigma_w - 1)^n - (A\sigma_w/\sigma^2)(1 + \mu\sigma)\right] \tag{10}$$

where

$\eta_w = (1/6)\pi\rho\sigma w^3 = \eta(1 - \eta/16), \eta$ being the packing fraction, and

$$g_o = g^{PY}(\sigma/\sigma_w, \eta_w) + A/\sigma,$$
$$g^{PY} = \xi_o(\eta_w) + \xi_1(\eta_w)(r/\sigma_w - 1) + (1/2)\xi_2(\eta_w)(r/\sigma_w - 1)^2,$$
$$A/\sigma = (3/4)\eta_w^2(1 - 0.7117\eta_w - 0.114\eta_w^2)/(1 - \eta_w)^4,$$
$$\xi_o = (1 + \eta_w/2)/(1 - \eta_w)^2$$
$$\xi_1 = (9/2)\eta_w(1 + \eta_w)/(1 - \eta_w)^3,$$
$$\xi_z = 3\eta_w(1 + 2\eta_w)^2/(1 - \eta_w)^4,$$
$$\mu\sigma = 24(A/\sigma\eta_2)(1 - \eta_w)^2/(1 + \eta_2/2)$$

3. RESULTS AND DISCUSSIONS

The choice of parametrization described above gives effective pair potentials which have shallow potential well with position of the first minimum shifted toward the large value of **r** in comparison to that of WH potential (see Figure 1). This is the feature an effective interionic interaction should have to represent a liquid transition metal as suggested by Hausleitner *et al*[17].

The results of $S(q)$ for the liquid transition metals near the melting points are presented in Figure 2. These have been compared here with the WCA and experimental results. The dashed line represents WCA, solid line LWCA and dots

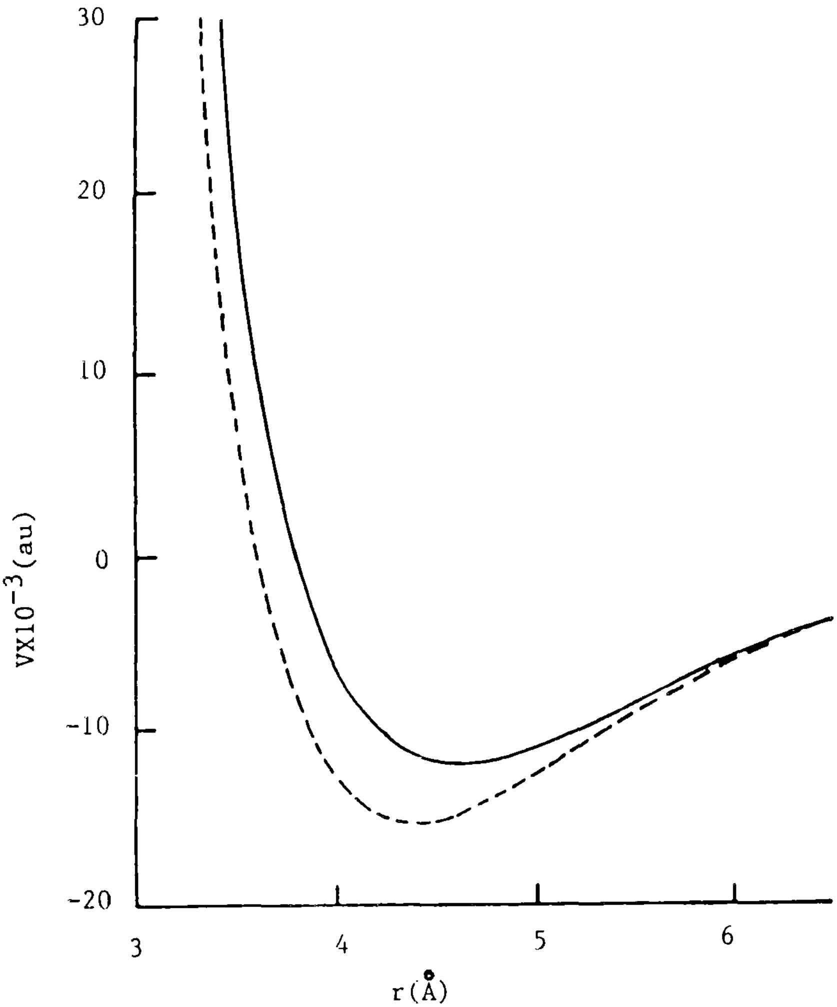

Figure 1 The effective pair potential for cobalt obtained from the WH[7] model. The solid and the broken curves respectively correspond to the present and Wills-Harrison parametrizations.

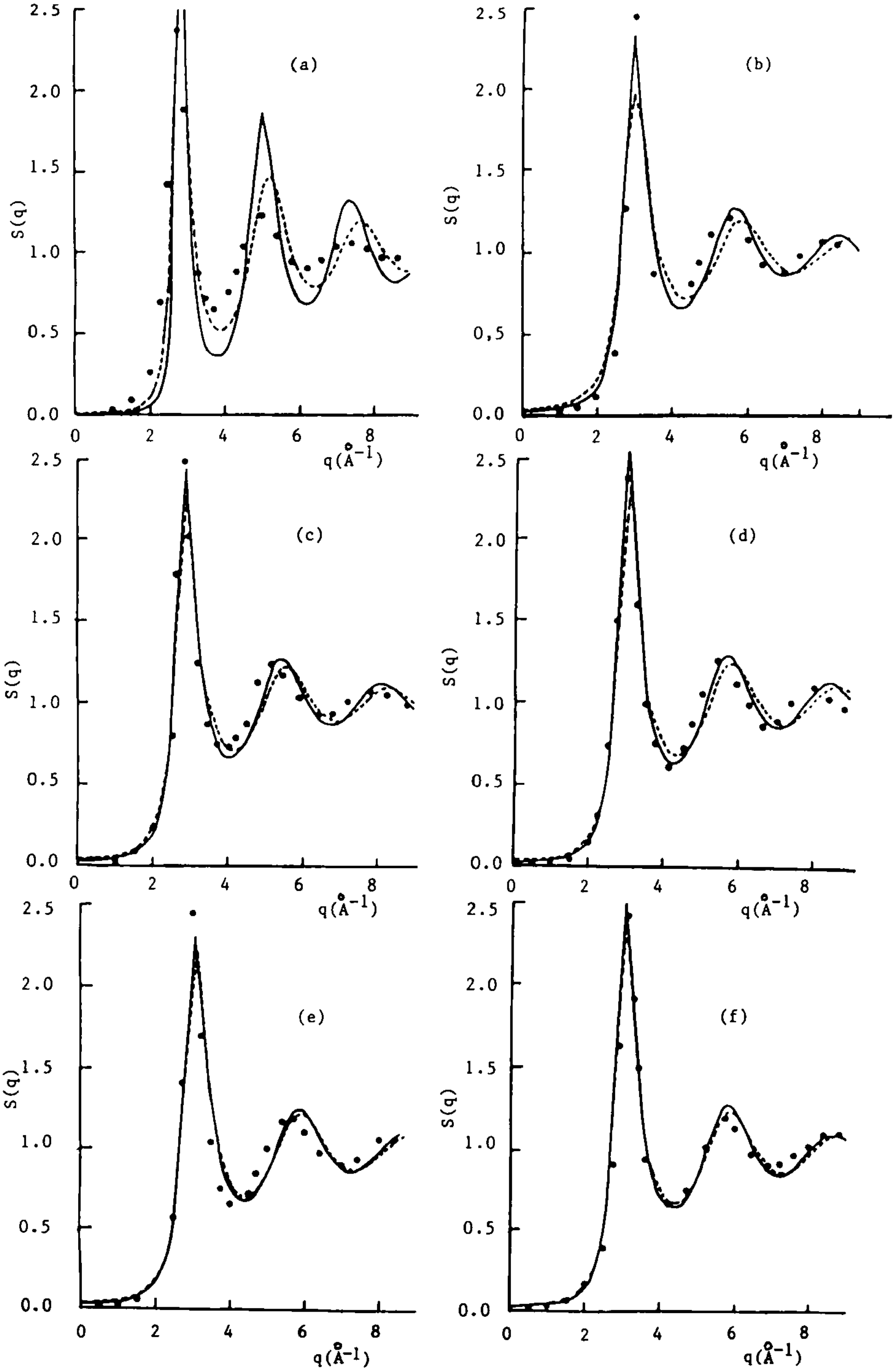

Figure 2 The static structure factor $S(q)$ for liquid transition metals near melting. The solid and the broken lines respectively correspond to the LWCA and WCA calculations. Here Fig. (a) represents V, (b) Cr, (c) Mn, (d) Fe, (e) Co and (f) Ni.

experimental results. From the figures it appears that except the early three 3d transition metals (Sc, Ti, V) agreement with X-ray diffraction data[23] is reasonably good. The height of the first peak of $S(q)$ is a little higher than the experimental results for Fe and Ni. For Cr, Mn and Co these are little lower. In the case of V, LWCA gives $S(q)$ which has exactly the same phase of oscillation but with relatively high peak values. For Sc and Ti peak values are much higher than those of experimental data and the oscillations are out of phase beyond the first peak and so we have not presented the figures for $S(q)$ for Sc and Ti in this report. It is also noticed that, for Sc, Ti and V both the WCA and LWCA predict packing fractions which are higher than the experimental values; this is reflected by the low-lying minima in the respective pair potentials. Perturbative calculations for $S(q)$ using the WH[19] and modified WH[18] in conjunction with the WCA-ORPA and WCA have also been unsuccessful for Sc, Ti and V. These calculations[18,19] also failed to produce reasonable results for $S(q)$ for elements in the middle of the 3d series in particular for Cr and Mn. In this respect LWCA with our parametrization has been proved to be relatively successful in the middle of the series.

When compared with experiments, the overall profiles of the present $S(q)$ for most of the 3d transition metals are found to be closer to experimental $S(q)$ than those found by the WCA calculations. In all cases the LWCA has shifted the oscillation of $S(q)$ toward the left with higher amplitudes relative to that of the WCA; this feature some what brings the present results closer to experiments[23]. Looking at the profiles of $V(r)$ (see Figure 1) it is observed that the well in the present pair potentials in all cases is shallower than the WCA based $V(r)$ and the minima in the present $V(r)$ are slightly shifted toward a larger value of **r**. This observation, reveals that the LWCA provides with higher packing fraction for each system than that provided by the WCA in a systematic way. Consequently other than the first three elements (see Table 2), the present calculations predict better packing fraction for the rest of the 3d series in comparison with the WCA. The WCA-ORPA calculations, however, yield comparable results; but the LWCA is still better in the middle of the series.

Our results for $S(q)$ calculated from the same potential in conjunction with LWCA and WCA also suggest that in liquid transition metals the position of the peak values beyond the first peak depends partly on the underlying liquid state theory and this has not been visible in the simple metals[6]. We also observed that the

Table 2 The calculated effective hard sphere diameter σ and the packing fraction η. The experimental η_{exp} have been obtained from ref. (23).

Element	$\sigma(au)$		η		η
	(LWCA)	*(WCA)*	*(LWCA)*	*(WCA)*	*(Expt)*
Sc	5.73	5.60	0.57	0.53	0.43
Ti	5.23	5.04	0.58	0.52	0.44
V	4.91	4.70	0.58	0.51	0.44
Cr	4.25	4.10	0.43	0.39	0.45
Mn	4.40	4.29	0.43	0.40	0.45
Fe	4.24	4.14	0.45	0.42	0.44
Co	4.10	4.05	0.42	0.41	0.45
Ni	4.15	4.09	0.44	0.42	0.45

difference between values of the effective hard sphere diameters for a particular system obtained from the LWCA and WCA increases when one goes from a harder to a softer potential[24]; this is expected from an energetic point of view.

In the perturbative calculations for liquid transition metals we have used only the repulsive part of the potential. It is an interesting problem to investigate why and how the results of $S(q)$ vary when different liquid state theories use a part or full effective pair potential obtained from the same model. This work is under investigation now and we shall report the results in due course.

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