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The Long-Wavelength Limit of the Structure Factor of Liquid 3d Transition Metals Using One-Component Plasma Model

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CONTENTS

ABSTRACT

The long-wavelength limit of the structure factor S(0) of liquid 3d transition metals has been calculated using the one-component plasma (OCP) model. Assuming that the interatomic forces can be expressed by the effective pair potential arising from the second-order pseudopotential theory, the structure factor S(k) in the small wavenumber k region is calculated using the random phase approximation (RPA) proposed by Chaturvedi et al. The present results for S(0) are in good agreement with the experimental data for all 3d transition metals near their melting points. This implies that the present approach involving various approximations to obtain the effective pair potential appears not to be severe for the basic understanding of the structural properties of 3d transition metals.

1. INTRODUCTION

In the last few years, there has been considerable progress in understanding the structure and thermodynamic properties of liquid metals using the classical one-component plasma (OCP) model, where the same density, temperature and ionic mass are employed as the real system. The OCP /1/ can be defined as a system of point particles, each carrying charge Ze, moving in a uniform neutralizing background. Such a system is characterized by an ion-sphere radius $a=(3/4\pi n)^{1/3}$, with n being the number density of ions, and a plasma parameter $\Gamma = (Ze)^2/ak_BT$.

The OCP model is first applied to liquid alkali metals /2-6/ and currently to liquid polyvalent metals /7,8/. On the other hand Itami and Shimoji /9/ have shown that the OCP model is also capable of describing the thermodynamic properties of liquid 3d transition metals close to the melting points. This approach has been further investigated by Itoh et al /10/ and its usefulness for transition metals is discussed in comparison with the results evaluated by the Percus-Yevick phonon model /11,12/. However, the detailed structural features have not yet been discussed.

The aim of this paper is to present the calculated low-angle structure factors and long-wavelength limits S(0) of liquid 3d transition metals using the OCP model. Here, the electron-ion interactions are assumed to be expressed by a low-order perturbative treatment like simple metals. All calculations in this paper are based on the random phase approximation (RPA) method proposed by Chaturvedi et al /5,6/.

2. CALCULATION PROCEDURE

As a first approximation to the electronic structure of a transition metal with Z valence electrons per ion, Z_d electrons are incorporated in the nonoverlapping ion core, the remaining $Z_s=Z-Z_d$ electrons per ion are in the free-electron-like states, and their coupling is considered to be weak. This idea of the separation between core and conduction electron states corresponds to the proposal by Wills and Harrison /13/, although the contribution by the d-electron is not explicitly taken into account here. Thus the calculation in this work should be considered a straightforward application of simple-metal theory. The effective interatomic pair potential $\phi(r)$ may be divided into the direct Coulomb repulsion between the bare ions $Z_s^2e^2/r$ and the screening contribution $\phi_{sc}(r)$:

$$\phi(r) = \frac{Z_s^2e^2}{r} + \phi_{sc}(r) \tag{1}$$

where e is the electronic charge. The $\phi_{sc}(r)$ term is assumed weak and considered as a perturbation to the structure arising from the bare Coulomb interaction between pair ions. The simplest approximation of $\phi_{sc}(r)$ for the structural function is known to be the RPA, so that

$$S(k) = S_{OCP}(k)\,[1+\beta n S_{OCP}(k)\phi_{sc}(k)]^{-1} \tag{2}$$

where $\beta=1/k_BT$ and $S_{OCP}(k)$ is the structure factor of the OCP at the same density and temperature as the real liquid metal and $\phi_{sc}(k)$ is the Fourier transform of $\phi_{sc}(r)$, given by

$$\phi_{sc}(k) = \chi(k)\upsilon(k)^2 \tag{3}$$

Here $\chi(k)$ is the density response function of the interacting homogeneous electron gas /14/ and $\upsilon(k)$ is a local pseudopotential describing the electron-ion interaction. This approach is true when $\phi_{sc}(k)$ is small. This will be the case /1,15/ for the electron-ion plasmas encountered in planetary interior and astrophysical problems. It is also the case for alkali metals at normal densities since the electron-ion pseudopotential $\upsilon(k)$ is weak. For example, Chaturvedi et al /5,6,16/ have shown that Eq. 2 describes well measured structure factors of liquid Na and K near the melting points. Their calculations also provide the realistic results for small k and some modification to $\phi_{sc}(k)$ produces good results for large values of k.

As for transition metals, it is generally accepted that the electron-ion interaction cannot be treated as a weak perturbation. Nevertheless, the simple-metal approach may be still applicable to these metals when the pseudopotential parameters are appropriately chosen as described in the next section. This proposition is well supported by the works of Regnaut et al /17,18/, although further investigation is still required. In the generalized pseudopotential theory formalism, the pair interionic interactions can be expressed, in atomic units (i.e., $m_e=\hbar=e=1$), by

$$\phi(r) = \frac{Z^{*2}}{r}\left[1-\frac{2}{\pi}\int F_N(k)\frac{\sin kr}{k}dk\right]+\phi^{ol}(r) \tag{4}$$

where $\phi^{ol}(r)$ is the overlap potential of d-electrons and Z* is the effective valence, given by

$$Z^{*}=Z+\frac{2}{(2\pi)^3 n}\int_{k>k_F}\sum_d\frac{\langle\vec{k}|\Delta|d\rangle\langle d|\Delta|\vec{k}\rangle}{(E_k-E_d)^2}\,d\vec{k}. \tag{5}$$

Here Δ denotes the hybridization operator, E_d is the mean d-band energy relative to the minimum energy of the free electron, and E_k is the free-electron kinetic energy. $F_N(K)$ is the energy-wavenumber characteristic given by Eq. 24 of Ref. 18. The simple-metal pair potential ($\Delta=0$, $\phi^{ol}(r)=0$) is modified by the s-d hybridization ($\Delta=0$, $\phi^{ol}(r)=0$) and by the overlap potential defined by Eq. 25 of Ref. 18. Based on the results of Regnaut et al for solid copper, the overlapping effect of ion cores almost cancels the hybridization effect at short range, leaving a simple metal-like pair potential. The net effect of the hybridization and overlapping of ion cores mainly appears in the long-range part of the pair potential, and such situation may be qualitatively true for liquid transition metals near their melting points.

According to Chaturvedi et al /6/, the long-wavelength limit of the structure factor S(0) of liquid metals can be written using Eqs. 2 and 3 as

$$S(0) = \left(\frac{k^2_{DH}}{k^2_e}+\frac{k^2_{DH}}{k^2_i}+k^2_{DH}r^2_c\right)^{-1} \tag{6}$$

where, in atomic units,

$$k_{DH} = (4\pi n Z^2_s/k_BT)^{1/2} \tag{7}$$

is the Debye-Hckel inverse screening length and k_i is the "inverse screening length" of the OCP, even though the quantity k^2_i given by

$$k^2_{DH}/k^2_i = 1-0.398415\Gamma+0.3122\Gamma^{1/4}-0.1850 \tag{8}$$

takes negative values at the temperatures and densities of the present interest. The quantity k_e in Eq. 6 is the inverse screening length of the electron gas and r_c is the Ashcroft core-radius for the electron-ion pseudopotential.

$$\upsilon(k) = -\frac{4\pi Z_s}{k^2}\cos(kr_c). \tag{9}$$

The screening function $\delta(k)$ may generally be expressed in terms of the local field correction $G(x)$ as

$$\varepsilon(k) = 1+\left(\frac{4k_F}{\pi k^2}\right)\frac{f(x)}{1-\frac{4k_F}{\pi k^2}G(x)f(x)}$$

with (10)

$$f(x) = \frac{1}{2}+\frac{x^2-1}{4x}\ln\left|\frac{1-x}{1+x}\right|, \quad x = \frac{k}{2k_F}.$$

The function $G(x)$ accounts for the exchange and correlation energies among the conduction electrons. Many forms of $G(x)$ have been proposed in the literature. The following three forms are used in this calculation: Geldart and Vosko (GV) /19/, Vashishta and Singwi (VS) /20/, and Ichimaru and Utsumi (IU) /21/.

The quantity k_e is related to $\epsilon(k)$ as

$$\lim_{k\to 0}\epsilon(k) = 1+\frac{k^2_e}{k^2} \tag{11}$$

and

$$k^2_e = \frac{4\pi k^3_F}{(\pi k_F)^2-\pi k_F-0.153} \quad \text{for GV,} \tag{12}$$

$$k_e^2 = \frac{4k_F^2}{\pi k_F - 4AB} \quad \text{for VS,} \tag{13}$$

$$k_e^2 = \frac{4k_F^2}{\pi k_F - 4\gamma_0} \quad \text{for IU,} \tag{14}$$

where $k_F = (3\pi^2 Z_s n)^{1/3}$, A and B are the density-dependent parameters tabulated in text of VS /20/, and γ_0 is also the density-dependent parameter defined in text of IU /21/.

3. RESULTS AND DISCUSSION

3.1. Calculations of Long-Wavelength Limit S(0)

In Table 1, the results of S(0) are summarized for liquid 3d transition metals near their melting points, together with the used parameters Γ and r_c. The values of Γ without bracket were taken from Itoh et al /10/, where the optimum values of Γ were determined by the OCP structure factors so as to fit the observed structure data around the first peak. On the other hand, the values of r_c are determined through the relation $k_0 r_c = \pi/2$. Here k_0 denotes the position of the first node of the Ashcroft pseudopotential in k space /22/ and are chosen to get the correct number of degrees of freedom, i.e., $k0 = (18\pi^2 n)^{1/3}$ /11,23/, in the manner similar to the method suggested by Yokoyama /24/ in describing the long-wavelength limit of the structure factor of liquid alkali metals. The values of r_c given in Table 1 are comparable to those of Wills and Harrrison (Table 1 of Ref. 13) obtained by minimizing the total energy, consisting of the free-electron energy, the d-band energy and the energy due to the shift in the d-band center, at the observed volume of each metal.

The calculated values of S(0) are rather surprisingly in excellent agreement with the experimental data recently reported by Waseda and Ueno /25/. The two screening functions GV and IU give much the same results but VS appears to give systematically large values of S(0). The calculated S(0) values are strongly affected by the plasma

TABLE 1

S(0) for liquid 3d transition metals near their melting temperatures as calculated from Eq. 6. ρ is the mass density, T the temperature, r_c the pseudopotential parameter and Γ the plasma parameter. For the meaning of other symbols see text.

	T	ρ	Γ	z*s	rc	S(0)			
						(calc)			(expt)**
	(K)	(g·cm^{-3})			(a.u.)	GV	VS	IU	
Ti	1973	4.15	110	1.47	1.413	0.0226	0.0236	0.0228	0.020
			(120)	1.53		0.0208	0.0217	0.0210	
V	2173	5.36	100	1.42	1.324	0.0234	0.0243	0.0236	0.025
Cr	2173	6.27	110	1.46	1.266	0.0205	0.0212	0.0207	0.021
Mn	1533	5.97	(100)	1.19	1.310	0.0231	0.0242	0.0233	0.024
			110	1.25		0.0211	0.0221	0.0213	
Fe	1833	7.01	110	1.33	1.249	0.0202	0.0210	0.0204	0.020
Co	1823	7.70	110	1.32	1.232	0.0199	0.0207	0.0201	0.019
Ni	1773	7.72	110	1.30	1.230	0.0199	0.0207	0.0201	0.020
Cu	1423	7.97	(130)	1.27	1.249	0.0172	0.0179	0.0173	0.018

* $Zs = \sqrt{\Gamma a k_B T}$

** taken from Waseda and Ueno /25/

parameter Γ. However, it may be worth mentioning that the plasma parameters used in this work can account fairly well for the observed entropies as well as the heat capacities at constant volume as is seen from Table 1 of Itoh et al /10/. Incidentally, the hard-sphere model is known to give much larger values of S(0) than the experimental ones (see, for example, Table 2 of Tamaki and Waseda /26/).

3.2. Comparison of Calculated and Measured S(K)

For very small k, Eq. 2 is expanded as

$$S(k) \approx \left[\frac{k_{DH}^2}{k_i^2} + \frac{k_{DH}^2(4+4k_e^2r_c^2-k_e^2r_c^4k^2)}{4(k^2+k_e^2)} \right]^{-1} \qquad (15)$$

Thus, the structure factors in low-k region can also be discussed. Using Eq. 2 for $1.4 \leq ka \leq k_0a = 3.5$ and Eq. 15 for $0 < ka < 1.4$, the structure factors were calculated up to k_0 using the three expressions of $G(x)$. The results are shown in Fig. 1 to Fig. 6 together with the experimental data /25,27/. As is seen from these figures, the observed low-k structure factors are moderately well described by the present method and good description is obtained for liquid Mn, Fe and Co, although there are small differences in detail in the region roughly between k_D and $k_0 = 3^{1/3}k_D$, where k_D is the radius of the conventional Debye sphere. The low-k structure factors are known to be severely influenced by the magnitude of Γ, in contrast with a little affected by the screening functions. On the other

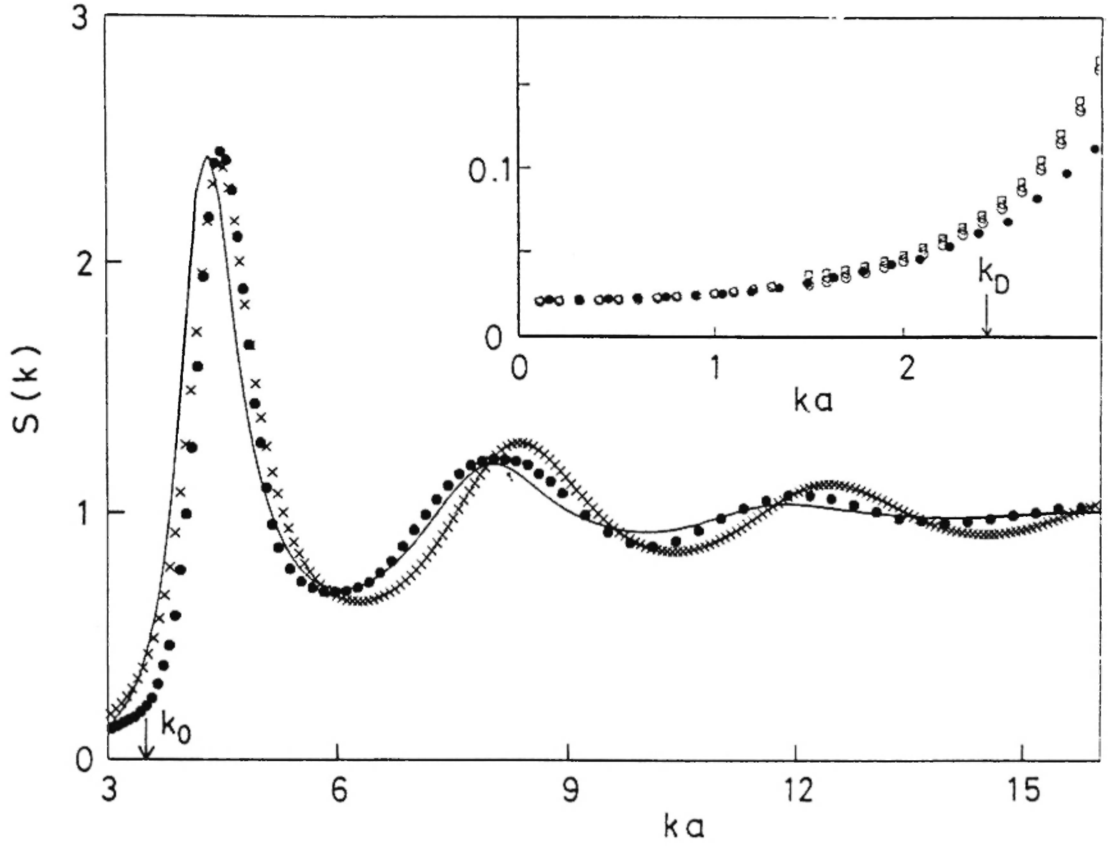

Fig. 1: Structure factors for liquid Cr at 2173 K. The full circles (●●●) denote the observed data (Waseda /27/, Waseda and Ueno /25/). The hard-sphere structure factors are shown with the crosses (xxx) using the packing fraction given in Ref. 26. The OCP structure factors (Roger et al /28/) for = 110 are shown with the full curve. The inset shows the calculated values in low-k region using Γ = 110 for three different dielectric functions GV(○), VS (Δ) and IU (□). The bare pseudopotential $\upsilon(k)$ is set to zero at $k_0 = 3^{1/3}k_D$ where k_D is the radius of the Debye sphere.

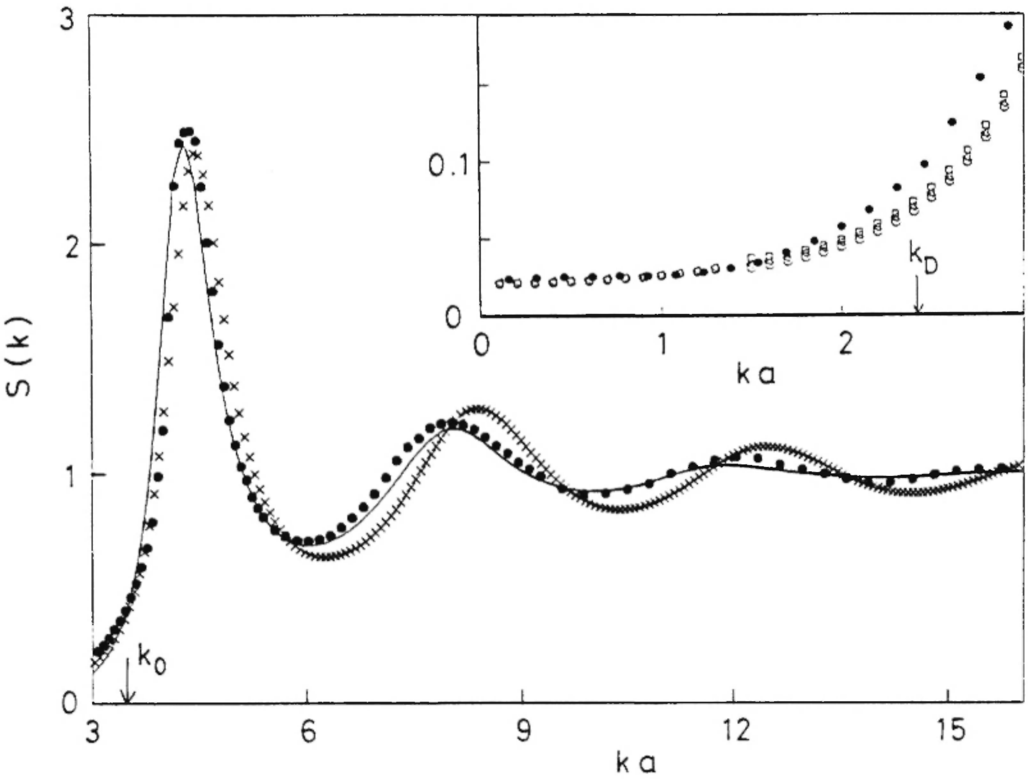

Fig. 2: As Figure 1, for liquid Mn at 1533 K using Γ = 110.

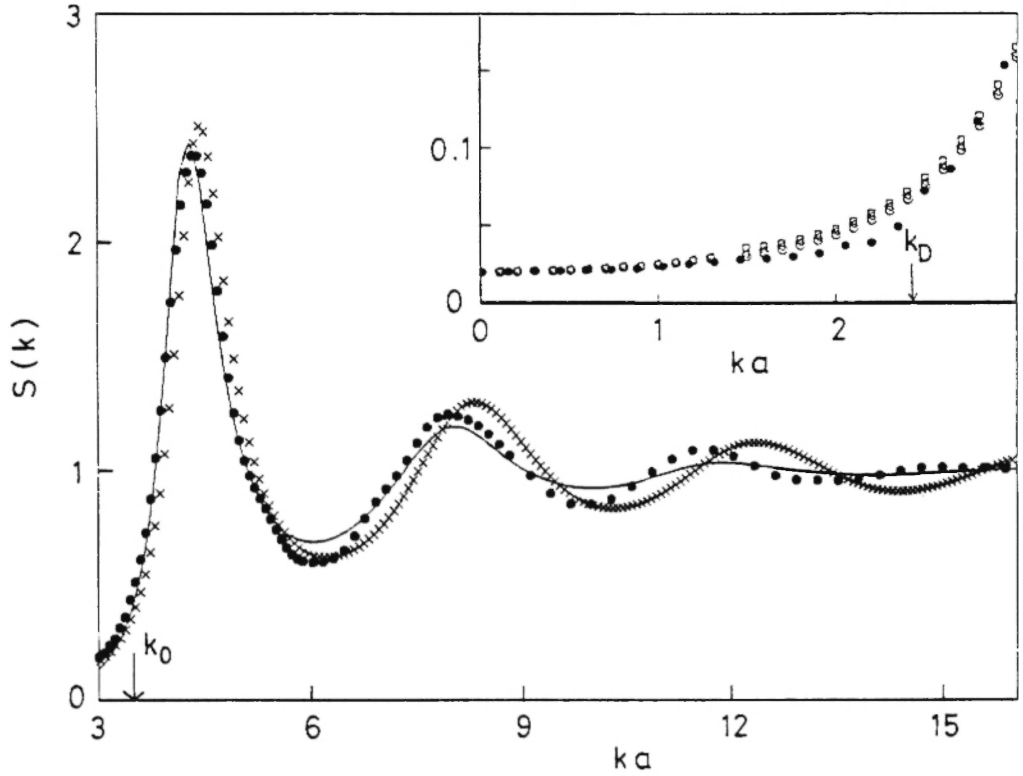

Fig. 3: As Figure 1, for liquid Fe at 1833 K using Γ = 110.

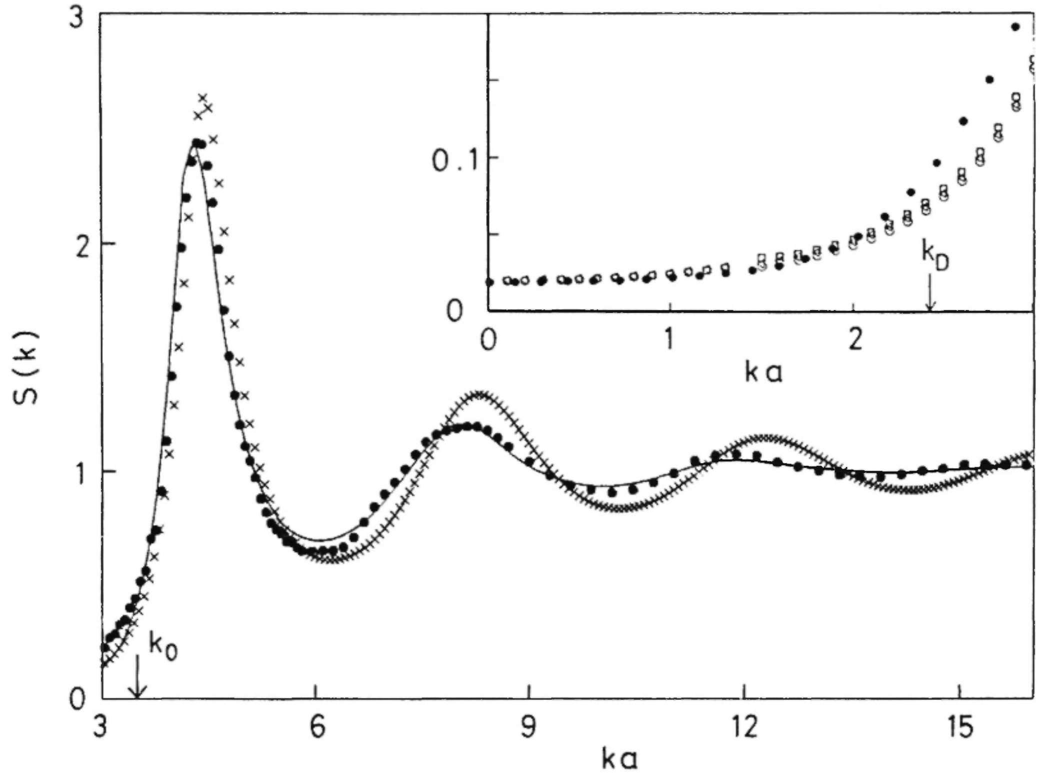

Fig. 4: As Figure 1, for liquid Co at 1823 K using Γ = 110.

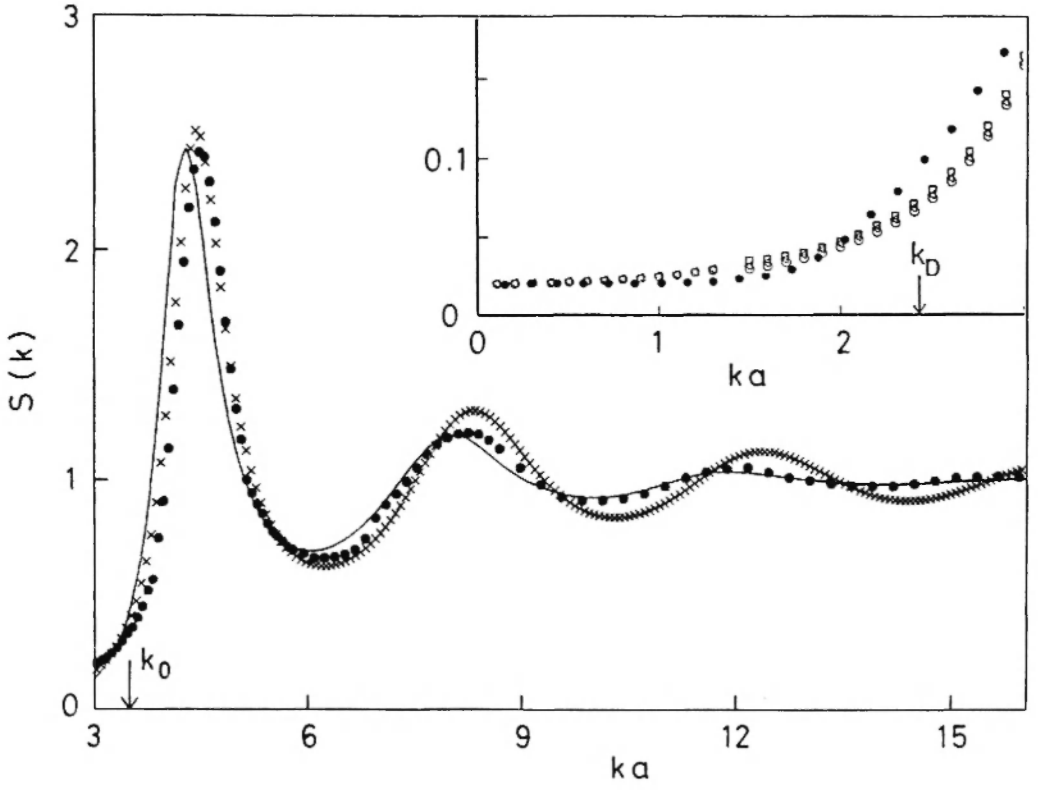

Fig. 5: As Figure 1, for liquid Ni at 1773 K using Γ = 110.

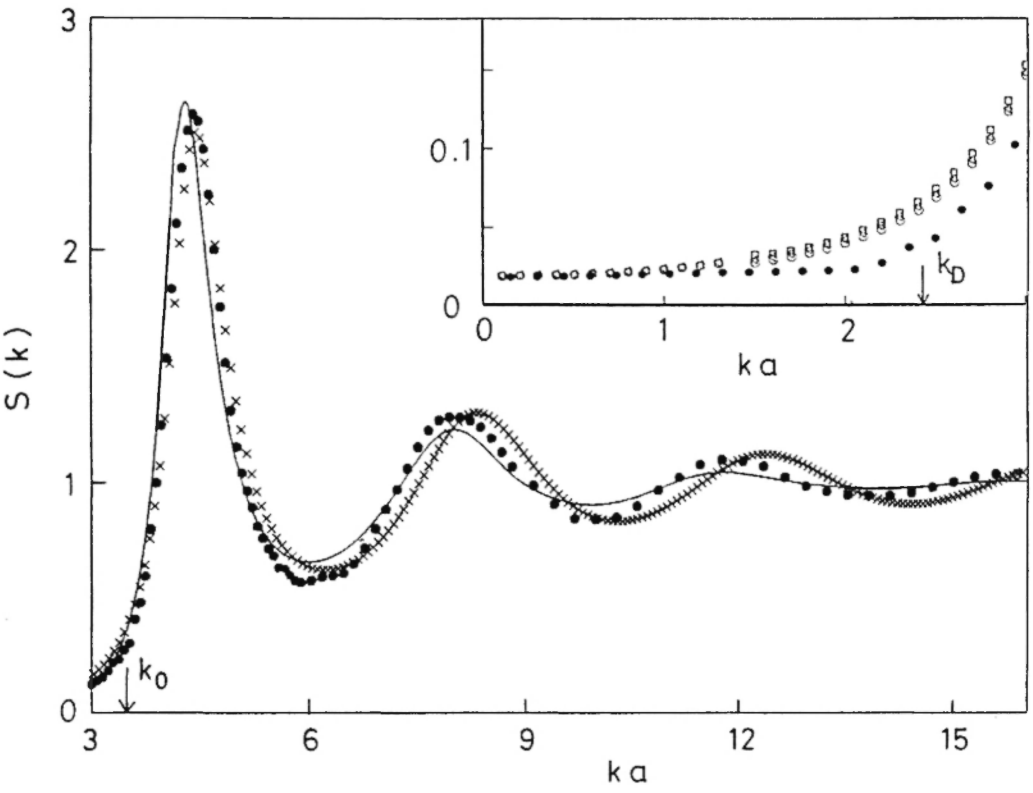

Fig. 6: As Figure 1, for liquid Cu at 1423 K using Γ = 130.

hand, the OCP structure factors /28/ in the high-k region are also displayed in these figures for comparison with the hard-sphere structure factors so as to see how they describe the real liquids. For the latter case, packing fractions are taken from Tamaki and Waseda /26/, while for the OCP, as has been done in Ref. 5, the bare electron-ion pseudopotential $\upsilon(k)$ is set to zero beyond its first node. This implies that the electron screening effect is essentially negligible in the region beyond k_0. Obviously, the gross features of the liquid structure are better described by the OCP model. The values of Γ determined by Itoh et al, therefore, are quite reasonable for describing the structure factors rather well in the wider k-region including the first peak to the higher k-region.

In conclusion, the OCP model using the RPA can predict the correct magnitude of the S(0) values and the low-k behaviour of liquid 3d transition metals near their melting points. However, the present approach does not involve the direct effects of the d-electrons and the s-d hybridization, and the relative number of s and d-electrons and the simple-metal theory are employed to describe the electron-ion interactions. Thus, some further consideration should be required about these approximations before the OCP model is recognized as a reliable tool for describing the structural properties of liquid 3d transition metals.

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