THE STRUCTURE OF
SIMPLE LIQUID METALS

A thesis submitted by

Marek Tadeusz Michalewicz

as complete fulfilment of the requirements for
the Degree of Master of Science
in the Division of Theoretical and Space Physics,
School of Physical Sciences,
La Trobe University, Melbourne, Australia

May 1984

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SUMMARY

The theory of the static structure factors of simple liquid metals is presented, and, in particular, the long-wavelenght limit of the structure factor is studied by means of the extended random phase approximation (ERPA) (Evans and Schirmacher, 1978) and Gaskell's approximation (GA) (Gaskell, 1978).

The theoretical structure factors for Rubidium (T=1900K, 350K, 313K), Aluminium (T=1330K, 978K, 943K) and Lead (T=613K) were computed. It was found that in all studied cases the contribution of the terms beyond random phase approximation (RPA) was smaller than 1%.

It is demonstrated that the Gaskell's approximation can be obtained by taking the second order MacLaurin expansion of the inverse structure factor about the reference fluid and neglecting the reminder term, instead of using the coupling-parameter formula and expansion of the integrand. This method is extended to the third order MacLaurin expansion. The extra term which is expressed in terms of the triple density correlation functions is given.

In order to obtain ERPA the theory of classical equilibrium statistical mechanics of inhomogenous liquids and the generating functional method are presented. The Weeks-Chandler-Andersen (WCA, 1971) theory and the 'blip' function method of Jacobs and Andersen (1975) were utilized to give the structure factor of the reference fluid.

The characteristic features of the simple liquid metals are incorporated by means of the effective pair-potential which represents interactions between pseudo-atoms.The model pseudopotential of Ashcroft (1968) and the dielectric function of Vashista and Singwi (1972) have been used to construct this potential.

TO MY WIFE, AGNIESZKA

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To conclude, I thank the University for granting me a Research Scholarship.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and to the best of the author's knowledge, it contains no material previously published or written by another person, except where due reference is made in the text.

M. T. Michalewicz

Marek Tadeusz Michalewicz

CHAPTER 1

INTRODUCTION

The aim of the thesis is to describe the low angle (i.e. long wavelength) structure factor of simple liquid metals using: i) the so-called Gaskell's approximation for the static structure factor, ii) the standard pseudopotential theory to obtain the interionic forces and iii) the theory of classical liquids to deduce the relevant structure properties.

We obtained the structure factor in low-k region for liquid Rubidium, Aluminuim and Lead in the Gaskell's approximation. The results are compared with calculations for two other models for the long wavelength structure factor - the random phase approximation (RPA) and the extended random phase approximation (ERPA).

In 1966 Ashcroft and Lekner used a solution of the Percus-Yevick equation for hard spheres (HS) to obtain a structure factor for some simple liquid metals. Their results agreed only moderately well with experiment. The 'blip' function theory of Weeks, Chandler and Andersen (1971) also utilized the hard sphere model. They divided the pair potential into a repulsive short range part and an attractive tail. The model liquid with only a repulsive short range interaction was called the soft sphere fluid. It can be used as a reference system for perturbation theories. The attractive, long range part of the potential plays the role of a perturbation. The WCA expression for the soft sphere liquid structure factor produced a spurious bump at low k and this defect was later corrected by Jacobs and Andersen, (JA), (1975).

The Jacobs and Andersen structure factor based on improved results for the hard sphere fluid (Verlet and Weis,1972) is, at the moment, one of the best available for the fluids with harsh repulsive potentials. The JA soft sphere structure factor reproduces the experimental values for real liquid metals well from about the second peak outwards (McLaughlin and Young,1982a).

In recent years some other types of reference systems for liquid metals have been intensively studied. One is called the one-component-plasma system (OCP), (Hansen,1973; Ross *et al*,1981; Mon *et al*,1981; Evans and Sluckin,1981; Iwamatsu *et al*,1982). It is described by the Coulombic part ($\psi_C=(Z^2e^2)/r$) of the effective pairwise interatomic potential derived from standard linear-screening theory (see Chapter 5). The OCP reference system has been applied successfuly for alkali liquid metals, but for polyvalent metals the HS reference system still plays a dominant role and gives better results (Mon *et al*,1981).

The other reference system, which is also of particular importance for alkalis, is called the charged hard spheres model (CHS). The important difference between the CHS and OCP is that in OCP ions are treated as point charges, whereas in CHS model ions are treated as objects of finite extension in space, (Hansen,1981). Singh and Holtz (1983) used CHS in their study on five liquid alkalis and found good agreement with experiment.

Another example of models applied in the liquid metal theory is the sticky hard sphere (SHS) liquid (Gopala Rao and Satpathy,1980). The structure factor for SHS liquid is obtained in analytical form, depends on two parametres and agrees with experiment reasonably well.

The WCA expression for the structure factor fails to describe the long wavelength range well. The notion that the tail of the pair-potential manifests its presence in the low-k region of the structure factor became generally accepted. There exist various perturbation theories that attempt to explain the role of the potential tail in this region.

The simplest of such theories, the random phase approximation (RPA) was for the first time applied in the study of liquid argon with a Lennard-Jones 6-12 potential by Woodhead-Galloway *et al*,(1968). Later in 1976 Henderson and Ashcroft in their study on binary mixtures derived an expression for the structure factor that is valid at long wavelength. It is called the mean-density approximation (MDA). The MDA was applied frequently in recent years in studies of liquid metal structure factors in the low-k range (McLaughlin *et al*.1981, McLaughlin and Young,1982a,b).

The MDA gives results which reproduce the characteristics and trends in real systems in the low-k region very well (McLaughlin and Young,1984a, b). Evans and Schirmacher (1978) have shown that by neglecting the density dependance of the radial distribution function in a derivation of the MDA one obtains a simpler formula. It was named by authors the extended random phase approximation (ERPA). They calculated the long wavelength limit of the structure factor for a number of insulating liquids and liquid metals.

Gaskell (1978) reported the derivation of yet another approximation for low angle structure factor. The Gaskell approximation (GA) is formally much simpler and easier to compute than the MDA and, although derived from quite different reasoning it resembles the ERPA. The only difference between the GA and the ERPA is the presence of an extra factor (S_0^2) in the integral term.

Recently Olsson and Dahlborg (1982) posed a problem of extracting a coarse form of the attractive part of the effective pair potential (or the perturbation part to a given reference potential) for liquid Al, Pb and Bi from the experimental low-k structure factor. They employed the GA, assuming its validity in the low angle range of the structure factor. They used the r^{-6} and r^{-12} reference system structure factor obtained from molecular dynamics simulations and also computed values for the hard sphere system. In order to model the perturbation part of the potential an elaborate expression, containing six adjustable parameters, was chosen. It consisted of a sum of a differentiated Gaussian function with a weight function displaceable along the r-axis and an exponential function. This combination of analytical expressions allowed very different shapes of the potential tail. It varied from a purely one-period oscillation to a simple exponential. They assumed that all kinds of oscillations of larger periodicity were damped out.

A similar approach to study the form of the potential tail was undertaken by Bretonnet (1983), but using the RPA. The liquid metal was modelled by the hard spheres supplemented with the oscillatory, exponentially decaying tail. This analytical model of the potential tail was proposed earlier by Cummings (1979). It depends on 5 adjustable parameters. Bretonnet, using the RPA, fitted experiments at low-k to find the effective pair potential for some liquid metals.

An alternative method of extracting the effective pair potential was proposed by McLaughlin and Young (1982c). In their approach, the long range part of the potential is derived from an observed structure factor and the RPA.

In contrast to the above approaches, the object of the present study was to test the validity of the Gaskell's approximation and so test the importance of the term representing the coupling of the density fluctuations of different wavevectors. This term expresses the correlation effects which are omitted in the RPA. In order to fulfill this purpose we applied the well accepted and tested effective pair potential derived from the pseudopotential theory. We used the simple, local, Ashcroft empty-core pseudopotential, which proved to be successful in simple liquid metals theory (Cohen and Heine, 1970). The screening of electrons was taken into account by means of Vashishta and Singwi (1972) form of the local field.

The calculated potential was separated according to the WCA prescription. Its short range part was used for computing the soft sphere reference system structure factor. The attractive long-range tail exhibited the typical oscillations. These, so-called Friedel oscillations, were included fully in all computations of the low-$\underline{k}$ structure factor.

The plan of the thesis is as follows. The relation between the radial distribution function, the total correlation function, the direct correlation function and the static structure factor is demonstrated in Chapter 2.

The hard sphere and the WCA soft sphere reference liquid models which were used in the present study are described in Chapter 3.

The development of the theories of the low angle structure factor will be presented in Chapter 4. In the second section of this chapter we present a new derivation of Gaskell's result. We extend this method to obtain the third order term in McLaurin expansion of the structure factor about the soft sphere reference system. The final expression is given in Appendix A. In Chapter 5 the effective pair potential for simple liquid metals is introduced.

In the last Chapter of this thesis the calculations of the small angle structure factor for liquid Rubidium (T=1900k, 350K, 313K), Aluminium (T=1330K, 978K, 943K) and Lead (T=613K) are presented. The results are presented graphically (Tables and Figures), and are discussed in detail. The last section (6.2) brings the final comments and conclusions.

CHAPTER 2

STATISTICAL MECHANICS OF LIQUID STATE

In this chapter we introduce some of the most important physical quantities of the classical statistical theory of dense fluids.We consider one-component monoatomic fluids in equilibrium described by canonical or grand canonical ensembles.

2.1 REDUCED DISTRIBUTION FUNCTIONS

The notions given here may be found in many standard textbooks (Rice and Gray,1965;Hansen and McDonald,1976 or Croxton,1974).In this paragraph we follow the presentation contained in (Balescu,1975).

In order to make our consideration more general we assume that the physical system is a member of an ensemble specified by a <u>phase-space distribution function</u>,$F(q,p)$,where $(q,p)=(q_1,..q_N,p_1,..p_N)$ are the generalized coordinates which span the phase-space of N particles.We do not specify any particular realization of the ensemble at the moment ,but require that

$$\int dqdpF(q,p)=1 \qquad (2.1.1)$$

and

$$F(q,p)\geqslant 0 \qquad (2.1.2)$$

The phase-space distribution $F(q,p)$ plays the role of the probability density of finding the system at point (q,p) in phase-space. It is postulated that any macroscopic quantity which is a function of physical space coordinates $\underline{x}$ and time t:$A(\underline{x},t)$

is a linear functional of a unique microscopic dynamical function $a(q,p,\underline{x},t)$.The link between the two is given by:

$$A(\underline{x},t)=\int dq dp\ \hat{a}(q,p,\underline{x},t)F(q,p)\equiv\langle\hat{a}\rangle \qquad (2.1.3)$$

where the integration is carried over the entire phase space.

Let us use the notation $x_i\equiv(\underline{q}_i,\underline{p}_i)$ for the set of canonical variables describing the i-th particle, and define <u>the reduced n-particle distribution function</u> $f_n(x_1,\ldots x_n)$ by the equation

$$f_n(x_1,..x_n)=\frac{N!}{(N-n)!}\int dx_{n+1}\ldots dx_N F(x_1,\ldots,x_n,x_{n+1},\ldots,x_N)$$

$$,n\leqslant N \qquad (2.1.4)$$

The reduced distribution functions are symmetric under permutations of the particles. This feature results from the assumption of the indistinguishibility of the particles of the system.

Another, equivalent way of defining f_n is:

$$f_n(y_1,\ldots,y_n)=\int dx_1..dx_N[\sum_{i_1}\ldots\sum_{i_n}\delta(y_1-x_{i_1})\delta(y_2-x_{i_2})..$$

$$\times\delta(y_n-x_{i_n})]F(x_1..x_N) \qquad (2.1.5)$$

According to the above expression the n-particle reduced distribution function may be treated as the n-point density in phase space.On the other hand <u>the number density</u> of particles in physical space is given by:

$$\rho(\underline{x})=\int dq dp \sum_{j=1}^{N} \delta(\underline{q}_j-\underline{x}) F(q,p) \qquad (2.1.6)$$

where $\hat{\rho}(\underline{x})=\sum_{j=1}^{N}\delta(\underline{q}_j-\underline{x})$ is density operator.

Similarly the two-point number density is defined by the expression:

$$\rho^{(2)}(\underline{x}_1,\underline{x}_2)=\int dq dp \sum_{\substack{j,n \\ j\neq n}}\sum \delta(\underline{q}_j-\underline{x}_1)\delta(\underline{q}_n-\underline{x}_2) F(q,p) \qquad (2.1.7)$$

The important point to note is that the integration in the formulas (2.1.6) and (2.1.7) is over the entire phase space.It is easy to show that in the canonical and the grand canonical ensembles the integration over momenta is immediately done due to particular forms of phase space distribution function and the hamiltonian.

Suppose the one-component system of N particles confined within the volume $\mathcal{V}$ has the hamiltonian:

$$H_N=T_N+U+V \qquad (2.1.8)$$

where the first term represents the kinetic energy

$$T_N=\sum_{i=1}^{N}\frac{p_i^2}{2m} \qquad (2.1.9)$$

of the particles of mass m and momentum p_i,and

$$U=U(\underline{q}_1,\ldots,\underline{q}_N) \qquad (2.1.10)$$

is the potential energy of interaction of particles

and

$$V=\sum_{i=1}^{N} v_{ext}(\underline{q}_i) \qquad (2.1.11)$$

is a contribution to the total configurational energy arising from the interaction of the particles with an external field.This last term often introduces spatial inhomogeneity in the system.

The phase space distribution function in the canonical ensemble for the system described by the hamiltonian given above is

$$F(q,p)=h^{-3N}(N!)^{-1}Z^{-1}\exp\{-\beta H_N(q,p)\} \qquad (2.1.12)$$

where $\beta=(k_BT)^{-1}$, k_B is the Boltzmann's constant, T is temperature and h-the Planck's constant.

Z is the partition function defined as

$$Z=h^{3N}(N!)^{-1}\int dqdp\ \exp\{-\beta H_N(q,p)\} \qquad (2.1.13)$$

The integration in the above formula with respect to the variables $p=(\underline{p}_1,\ldots,\underline{p}_N)$ yields factorization:

$$Z=Z_TQ \qquad (2.1.14)$$

where Z_T is the partition function of the ideal Boltzmann gas (classical system of particles without interactions)

$$Z_T=(N!)^{-1}\nu^N\Lambda^{-3N} \qquad (2.1.15)$$

and $\Lambda=(\frac{2\pi\beta\hbar^2}{m})^{\frac{1}{2}}$ is called de Broglie thermal wavelength. The genuinely interesting factor in formula (2.1.14) is Q-the configurational integral given by

$$Q(T,V,N)=\nu^{-N}\int dq\ \exp\{-\beta(U+V)\} \qquad (2.1.16)$$

We may apply formulas (2.1.12)-(2.1.15) together with the general definition of the reduced distribution function (2.1.4) in order to obtain one and two-particle reduced distribution functions in the canonical ensemble:

$$f_1(\underline{q}_1,\underline{p}_1)=\rho(\underline{q}_1)\rho(p_1) \qquad (2.1.17)$$

here $\rho(p)$ is the Maxwell distribution of momenta

$$\rho(p)=\left(\frac{\beta}{2\pi m}\right)^{3/2}\exp\{-\beta\frac{p^2}{2m}\} \qquad (2.1.18)$$

and

$$\rho(q)=NV^{-N}Q^{-1}\int d\underline{q}_2\ldots d\underline{q}_N\ \exp\{-\beta(U+V)\} \qquad (2.1.19)$$

is the configurational one particle density. The two-body reduced distribution function is found to be:

$$f_2(\underline{q}_1,\underline{q}_2,\underline{p}_1,\underline{p}_2)=\rho^{(2)}(\underline{q}_1,\underline{q}_2)\rho(p_1)\rho(p_2) \qquad (2.1.20)$$

The function $\rho^{(2)}(\underline{q}_1,\underline{q}_2)$ is sometimes called the configurational two-body distribution. It can be demonstrated that in a fluid phase in equilibrium the one particle density is constant:

$$\rho(q)=\rho=\frac{N}{V} \qquad (2.1.21)$$

One can easily check the following properties of one and two-body distribution functions:

$$\int d\underline{p}_1 f_1(\underline{q}_1,\underline{p}_1)=\rho(\underline{q}) \qquad (2.1.22)$$

and

$$\int d\underline{p}_1 d\underline{p}_2\ f_2(\underline{q}_1,\underline{q}_2,\underline{p}_1,\underline{p}_2)=\rho^{(2)}(\underline{q}_1,\underline{q}_2) \qquad (2.1.23)$$

Obviously the expressions (2.1.22) and (2.1.23) are equivalent to the definitions (2.1.6) and (2.1.7) respectively. The two-body distribution function plays the central role in liquid state theory, usually it is represented in terms of the <u>pair</u> <u>distribution</u> <u>function</u> $g(\underline{q}_1,\underline{q}_2)$:

$$\rho^{(2)}(\underline{q}_1,\underline{q}_2)=\rho^2 g(\underline{q}_1,\underline{q}_2) \qquad (2.1.24)$$

In the case of homogeneous fluid due to translational invariance the pair distribution function may be written

$$g(\underline{q}_1,\underline{q}_2)=g(|\underline{r}_1-\underline{r}_2|)=g(r_{12}) \qquad (2.1.25)$$

and is then called the radial distribution function (Hansen and McDonald,1976).

It can be interpreted as a probability of finding a particle at the distance r from another particle at the origin.Clearly,it possesses the property:

$$\lim_{r\to\infty} g(r)=1 \qquad (2.1.26)$$

It is customary (Ashcroft and Stroud,1978) to introduce the total correlation function , h(r), at this point ,by the equation:

$$h(r)=g(r)-1 \qquad (2.1.27)$$

with the obvious property

$$\lim_{r\to\infty} h(r)=0 \qquad (2.1.28)$$

From Eq.(2.1.27) we see that h(r) expresses the entire effect of correlations. It can be demonstrated (Hansen and McDonald,1976; Balescu,1975), that the total correlation function is related to the isothermal compressibility χ_T,via so called the compresibility equation:

$$1+\rho\int h(\underline{r})d\underline{r}=\rho\beta^{-1}\chi_T \qquad (2.1.29)$$

This interesting equation is very useful in the theory of the equation of state of dense liquids.Its relevance to the theory of the structure factor will be shown later.

2.2 DIRECT CORRELATION FUNCTIONS

In this subchapter we introduce the concept of direct correlation functions.The style of presentation adopted is similar to this given by (Evans,1979).The systems studied here are the classical ,monoatomic ,one-component ,non-uniform fluids. We use the grand canonical ensemble which is more suitable for the generating functional method (Lebowitz and Percus,1963).

Let us assume that the system is described by the hamiltonian H_N ,given by Eqs.(2.1.8)-(2.1.11).The number of particles N in the system may fluctuate and the equilibrium phase space distribution for N particles is:

$$F_0=\Xi^{-1}\ \exp\{-\beta(H_N-\mu N)\} \qquad (2.2.1)$$

where μ is the chemical potential and Ξ is the grand partition function:

$$\Xi=\mathrm{Tr}_{cl}\ \exp\{-\beta(H_N-\mu N)\} \qquad (2.2.2)$$

Tr_{cl} is an operator of the form:

$$\mathrm{Tr}_{cl}\equiv\sum_{N=0}^{\infty}(h^{3N}N!)^{-1}\int d\underline{r}_1\ldots d\underline{r}_N\int d\underline{p}_1\ldots d\underline{p}_N \qquad (2.2.3)$$

Similarily as in the previous section ,(2.1.3), we define the grand canonical ensemble average of a microscopic dynamical function $\hat{a}(q,p,\underline{x},N,t)$ to be

$$\langle\hat{a}\rangle\equiv\mathrm{Tr}_{cl}F_0\hat{a} \qquad (2.2.4)$$

It can be shown (Evans,1979) that any functional of the given phase space distribution may be treated as a unique functional of the density $\rho(\underline{r})$.

We construct two functionals which occupy a central position in the development of the theory.The first is the intrinsic Helmholtz free energy of the system:

$$F[\rho]=\langle T_N+U+\beta^{-1}\ln F_o\rangle \qquad (2.2.5)$$

The other is written:

$$\Omega_V[\rho]=\int d\underline{r}\rho(\underline{r})V_{ext}(\underline{r}) + F[\rho] - \mu\int d\underline{r}\rho(\underline{r}) \qquad (2.2.6)$$

It can be demonstrated that the equilibrium density $\rho_0(\underline{r})$ (corresponding to F_0) minimizes the above expression and gives the grand thermodynamic potential Ω:

$$\left.\frac{\delta\Omega_V[\rho]}{\delta\rho(\underline{r})}\right|_{\rho_0} = 0 \qquad (2.2.7)$$

and

$$\Omega_V[\rho_0]=-\beta^{-1}\ln\Xi \equiv \Omega \qquad (2.2.8)$$

From Eqs.(2.2.6) and (2.2.7) we immediately obtain the important result of the theory of non-uniform fluids:

$$\mu=V_{ext}(\underline{r})+\mu_{in}[\rho_0;\underline{r}] \qquad (2.2.9)$$

where

$$\mu_{in}[\rho;\underline{r}]\equiv\frac{\delta F[\rho]}{\delta\rho(\underline{r})} \qquad (2.2.10)$$

is the intrinsic chemical potential.In the case of non-interacting systems (U=0) Eq.(2.2.5) reduces to

$$F_{id}[\rho]=\beta^{-1}\int d\underline{r}\rho(\underline{r})\{\ln(\Lambda^3\rho(\underline{r}))-1\} \qquad (2.2.11)$$

where Λ is de Broglie thermal wavelength (2.1.15).For the given potential U the effects of the particle interactions can be incorporated by the unique functional of $\rho(\underline{r})$,$\Phi[\rho]$.

Now the expression (2.2.5) is rewritten:

$$F[\rho] \equiv F_{id}[\rho] + \Phi[\rho] \tag{2.2.12}$$

We define the first member of the hierarchy of the direct correlation functions by:

$$c[\rho;\underline{r}] \equiv \beta \frac{\delta\Phi[\rho]}{\delta\rho(\underline{r})} \tag{2.2.13}$$

From Eqs.(2.2.10)-(2.2.13) one gets

$$\beta\mu_{in}[\rho;\underline{r}]=\ln(\Lambda^3\rho(\underline{r}))-c[\rho;\underline{r}] \tag{2.2.14}$$

This result applied together with Eq.(2.2.9) gives the equilibrium density of non-uniform fluid $\rho_0(\underline{r})$ in terms of a given external potential $V_{ext}(\underline{r})$ and fugacity $z=\Lambda^{-3}\exp\{\beta\mu\}$:

$$\rho_0(\underline{r})= z \exp\{-\beta V_{ext}(\underline{r}) + c[\rho_0;\underline{r}]\} \tag{2.2.15}$$

Eq.(2.2.15) provides an interpretation of the meaning of $c[\rho;\underline{r}]$ as the additional, effective one-body potential which determines the equilibrium density in a self-consistent way (Evans,1979).

The most important of the higher order direct correlation functions generated by $\Phi[\rho]$ is

$$c[\rho;\underline{r}_1,\underline{r}_2] = \frac{\delta c[\rho;\underline{r}_1]}{\delta\rho(\underline{r}_2)} = \beta\frac{\delta^2\Phi[\rho]}{\delta\rho(\underline{r}_1)\delta\rho(\underline{r}_2)} \tag{2.2.16}$$

This function taken for the equilibrium density is called the Ornstein-Zernike direct correlation function of the non-uniform fluid.It can be represented as

$$c^{(2)}(\underline{r}_1,\underline{r}_2) \equiv c[\rho_0;\underline{r}_1,\underline{r}_2]= \frac{\delta(\underline{r}_1-\underline{r}_2)}{\rho_0(\underline{r}_1)} - \beta\frac{\delta u(\underline{r}_1)}{\delta\rho_0(\underline{r}_2)} \tag{2.2.17}$$

where $u(\underline{r})=\mu-V_{ext}(\underline{r})$ and Eqs.(2.2.15)-(2.2.16) were used.

The grand thermodynamic potential (2.2.8) is a generating functional for the configurational densities (Balescu,1975):

$$\frac{\delta\Omega}{\delta u(\underline{r})} = -\rho_0(\underline{r}) \qquad (2.2.18)$$

Differentiating this equation again we obtain the density-density correlation function or the density fluctuation $G(\underline{r}_1,\underline{r}_2)$:

$$\beta^{-1}\frac{\delta\rho_0(\underline{r}_1)}{\delta u(\underline{r}_2)}=<[\hat{\rho}(\underline{r}_1)-\rho_0(\underline{r}_1)][\hat{\rho}(\underline{r}_2)-\rho_0(\underline{r}_2)]>=G(\underline{r}_1,\underline{r}_2) \qquad (2.2.19)$$

It is easy to prove (Balescu,1975),that the density fluctuation is related to the two-body density via the equation:

$$G(\underline{r}_1,\underline{r}_2)=\rho^{(2)}(\underline{r}_1,\underline{r}_2)+\rho_0(\underline{r}_1)\delta(\underline{r}_1-\underline{r}_2)-\rho_0(\underline{r}_1)\rho_0(\underline{r}_2) \qquad (2.2.20)$$

We substitute this representation , together with (2.2.17) into the equation defining the inverse $G^{-1}(\underline{r}_1,\underline{r}_2)=\beta\frac{\delta u(\underline{r}\ )}{\delta\rho_0(\underline{r}_2)}$:

$$\int d\underline{r}_3 G^{-1}(\underline{r}_1,\underline{r}_3)G(\underline{r}_3,\underline{r}_2)=\delta(\underline{r}_1-\underline{r}_2) \qquad (2.2.21)$$

and we obtain the integral equation:

$$\rho^{(2)}(\underline{r}_1,\underline{r}_2)-\rho_0(\underline{r}_1)\rho_0(\underline{r}_2)=\rho_0(\underline{r}_1)\rho_0(\underline{r}_2)c^{(2)}(\underline{r}_1,\underline{r}_2)$$
$$+\ \rho_0(\underline{r}_2)\int d\underline{r}_3(\rho^{(2)}(\underline{r}_1,\underline{r}_2)-\rho_0(\underline{r}_1)\rho_0(\underline{r}_3))c^{(2)}(\underline{r}_3,\underline{r}_2) \qquad (2.2.22)$$

This reduces to the famous Ornstein-Zernike equation (Ornstein and Zernike,1914) in a case of a uniform fluid of density ρ_0:

$$h(r)=c^{(2)}(r) + \rho_0\int d\underline{r}_1 h(r_1)c^{(2)}(|\underline{r}-\underline{r}_1|) \qquad (2.2.23)$$

where we used definitions (2.1.24),(2.1.25) and (2.1.27).

The physical interpretation of the direct correlation function follows from the above formula .

The total correlation function which represents the entire effect of correlations in fluid is separated into direct correlation between the particle at the origin and the other one at the distance r from it , and the convolution of the correlation between all the particles of the fluid and the one at r.The vital property of $c^{(2)}(r)$ is its range comparable with the range of the pair-potential.The Ornstein-Zernike equation is exact but it can be solved only if the provisional independent relation between the total and direct correlation functions is given.One of the most successful closure relations in liquid state theory is Percus-Yevick formula which will be discussed briefly in the next chapter.

2.3 THE STATIC STRUCTURE FACTOR

In equilibrium classical statistical mechanics the knowledge of the partition function ,(2.1.13) or (2.2.2) ,enables one to calculate the thermodynamic potentials and hence from it by algebraic operations or by differentiations all other thermodynamic functions (Balescu,1975). In the theory of dense fluids however it is the pair distribution function (2.1.24), not the partition function, which plays the most important role.

Let us make the most common and essential assumption at this point that the potential energy of interaction of particles in a liquid, (2.1.10), is the sum of pair-wise potentials $\psi(\underline{r})$:

$$U(\underline{r}_1,\ldots,\underline{r}_N) = \sum_{1\leq i<j\leq N} \psi(\underline{r}_{ij}) \qquad (2.3.1)$$

With the above assumption the thermodynamic functions of the liquid such as the internal energy, the specific heat per molecule at constant volume, pressure (via the equation of state) and others are expressed as functionals of the pair distribution function and the pair-potential (or their derivatives), (Egelstaff,1967).

Another very important feature of the pair distribution function is that it can be determined experimentally.The structure of liquids is studied experimentally by means of X-ray, neutron and electron diffraction (Waseda,1980).Suppose the incident and scattered X-rays have wave-vectors $\underline{k}_i$ and $\underline{k}_f$ respectively.

The momentum transfer is then $\underline{k}=\underline{k}_f-\underline{k}_i$ and we write the amplitude of the scattered X-rays as:

$$A(\underline{k})=\sum_{i=1}^{N} f_i(\underline{k})\exp\{-i\underline{k}\cdot\underline{r}_i\} \qquad (2.3.2)$$

where $f_i(\underline{k})$ is the atomic scattering factor for the i-th atom located at position $\underline{r}_i$. The measured intensity of the wave scattered by N particles forming the one-component fluid is the ensemble average of the absolute square of the amplitude (2.3.2):

$$I(\underline{k})=\langle|A(\underline{k})|^2\rangle=|f(k)|^2\langle \sum_j \sum_n \exp\{-i\underline{k}\cdot(\underline{r}_j-\underline{r}_n)\}\rangle \qquad (2.3.3)$$

This can be written:

$$I(\underline{k}) = |f(k)|^2 NS(\underline{k}) \qquad (2.3.4)$$

where the function

$$S(\underline{k}) \equiv N^{-1}\langle(\sum_j\exp\{-i\underline{k}\cdot\underline{r}_j\})(\sum_n\exp\{i\underline{k}\cdot\underline{r}_n\})\rangle \qquad (2.3.5)$$

is called <u>the static structure factor</u> or simply the structure factor. It is easy to notice that the Fourier transform of the density operator $\hat{\rho}(\underline{r})=\sum_{j=1}^{N}\delta(\underline{r}_j-\underline{r})$ is

$$\rho_{\underline{k}}=\int d\underline{r}\ \exp\{-i\underline{k}\cdot\underline{r}\}\hat{\rho}(\underline{r}) = \sum_{j=1}^{N}\exp\{-i\underline{k}\cdot\underline{r}_j\} \qquad (2.3.6)$$

and now the structure factor (2.3.5) can be interpreted as the autocorrelation function of the particle density in $\underline{k}$-space.

We write it

$$S(\underline{k}) \equiv N^{-1}\langle\rho_{\underline{k}}\rho_{-\underline{k}}\rangle \qquad (2.3.7)$$

It is convenient to redefine the definition (2.3.5) or (2.3.7). We exclude the contribution which corresponds to the forward scattering of radiation ($\underline{k}$=0). Now Eqs.(2.3.5) and (2.3.7) are written

$$S(\underline{k}) = N^{-1}\langle \sum_j \sum_n \exp\{-i\underline{k}\cdot(\underline{r}_j-\underline{r}_n)\}\rangle - N\delta_{\underline{k},0} \qquad (2.3.5a)$$

and

$$S(\underline{k}) = N^{-1}\langle \rho_{\underline{k}}\rho_{-\underline{k}}\rangle \quad ,\underline{k}\neq 0 \qquad (2.3.7a)$$

One easily finds the fundamental relation between the pair distribution function and the structure factor (Hansen and McDonald,1976; Balescu,1975; Waseda,1980). In order to do this we separate the terms for which j=n in Eq.(2.3.5a) and write

$$S(k) = 1+N^{-1}\int d\underline{r}d\underline{r}'\ \exp\{-i\underline{k}\cdot(\underline{r}-\underline{r}')\}\langle \sum_j \sum_{\substack{n \\ j\neq n}} \delta(\underline{r}-\underline{r}_j)\delta(\underline{r}'-\underline{r}_n)\rangle - N\delta_{\underline{k},0} \qquad (2.3.8)$$

Now we recall Eqs.(2.1.7) and (2.1.24) and use the equivalence

$$\delta_{\underline{k},0} = V^{-1}\int d\underline{r}\ \exp\{-i\underline{k}\cdot\underline{r}\} \qquad (2.3.9)$$

and the equation (2.3.8) for isotropic system becomes

$$S(k) = 1 + \rho\int d\underline{r}\ \exp\{-i\underline{k}\cdot\underline{r}\}[g(r)-1] \qquad (2.3.10)$$

or

$$S(k) = 1 + \rho\hat{h}(k) \qquad (2.3.11)$$

where $\hat{h}(k)$ is the Fourier transform of the total correlation function defined by Eq.(2.1.27). We observe that the structure factor is the Fourier transform of the total correlation function. One immediately obtains the reciprocal relation:

$$g(r)-1 = (2\pi)^{-3}\rho^{-1}\int d\underline{r}[S(k)-1]\exp\{i\underline{k}\cdot\underline{r}\} \qquad (2.3.12)$$

From the compressibility equation (2.1.29) and the formula (2.3.10) we find the value of the structure factor for k=0 :

$$S(0) = \rho\beta^{-1}\chi_T \qquad (2.3.13)$$

The experimental values of the isothermal compressibility χ_T can be obtained from measurements of the sound velocity and the ratio of specific heats and hence the formula (2.3.13) provides an independent experimental test of the zero k limit of the structure factor obtained from diffraction experiments or the theory (Evans and Schirmacher,1978).

The Fourier transform of the Ornstein-Zernike equation (2.2.23) together with Eq.(2.3.11) yields the link between S(k) and the direct correlation function:

$$S(k) = \{1-\rho\hat{c}(k)\}^{-1} \qquad (2.3.14)$$

If the system is subjected to a weak external potential then the linear density response is related to the structure factor by the equation (Hansen and McDonald, 1976; Ashcroft and Stroud, 1978):

$$S(k) = -(\rho\beta)^{-1}\chi(k,0) \qquad (2.3.15)$$

where $\chi(k,\omega)$ is the linear response function.

CHAPTER 3

THE WCA REFERENCE FLUID

The successful development of the theory of liquids in the last two decades rests on the van der Waals idea that the model system with the harsh repulsive forces will exhibit most of the thermodynamic and structural features of a real system. The simplest and yet nontrivial model system is the hard sphere fluid.

3.1 THE HARD SPHERE FLUID

In their well known paper Percus and Yevick (1958) established the approximate relation between the radial distribution function (2.1.25) and the pair potential (2.3.1). Their result was later rederived by a graph summation method (Stell,1963) and by a generating functional method (Lebowitz and Percus,1963). Following the latter approach one can expand the ingeniously chosen generating functional $A(\underline{r};\Psi)=\rho(\underline{r};\Psi)\exp\{\beta\psi_{01}\}$,where Ψ is the interaction of an extra (N+1) particle with the N particle system and $\psi_{01}=\psi(\underline{r}_{(N+1)1})$, in powers of the functional $B(\underline{r};\Psi)=\rho(\underline{r};\Psi)$. The expansion, truncated at the linear term and combined with (2.2.20) ,(2.2.17) (where $u=\Psi$) and (2.2.23) after some manipulation yields the relation between the radial distribution function and the direct correlation function (Balescu,1975):

$$c(r)=[1-\exp\{\beta\psi(r)\}]g(r) \qquad (3.1.1)$$

This is the Percus-Yevick closure formula which can be used to solve the Ornstein-Zernike equation (2.2.23).

The resulting equation is called the Percus-Yevick equation (P-Y) and is written

$$g(r)\exp\{\beta\psi(r)\} = 1 - \rho\int d\underline{r}'[\exp\{\beta\psi(r')\}-1]g(r') \times[g(|\underline{r}-\underline{r}'|)-1] \qquad (3.1.2)$$

This nonlinear integral equation for the radial distribution function is one of the best available in the liquid state theory. The reason is twofold.

Firstly, the P-Y solutions for various model systems (e.g. hard spheres, Lennard-Jones) consistently are closer to the results of computer experiments then other approximations. They give consistent pressure and compressibility equations of state for hard spheres and better numerical values of fourth and higher virial coefficients over the wide range of densities then other approximate analitical expressions like hypernetted-chains equation (HNC). Secondly, there exist rigorous solution for the special but very important case of a hard sphere fluid. The solution was obtained independently by Wertheim (1963a,b) and Thiele (1963),(W-T).

They consider the fluid of hard spheres defined by the pair potential of the form:

$$\begin{aligned} \psi_\sigma(r) &= +\infty \qquad r<\sigma \\ \psi_\sigma(r) &= 0 \qquad r>\sigma \end{aligned} \qquad (3.1.3)$$

where σ is the diameter of the hard spheres.

Due to the singular form of the potential and from (3.1.1) one obtains:

$$
\begin{aligned}
&g_{\sigma}(r)=0 && r<\sigma,\\
&g_{\sigma}(r)=\tau_{\sigma}(r) && r>\sigma,\\
&c(r)=-\tau_{\sigma}(r) && r<\sigma,\\
&c(r)=0 && r>\sigma
\end{aligned}
\qquad (3.1.4)
$$

where

$$\tau_{\sigma}(r)=\exp\{\beta\psi_{\sigma}(r)\}g_{\sigma}(r) \qquad (3.1.5)$$

Rewritting the P-Y equation in bipolar coordinate system and Laplace-transforming it one achives the factorization in terms of the functions of a complex argument. One exploits the properties of the entire functions and after considerable calculations one obtains the direct correlation function for the fluid of hard spheres:

$$c(r^{*})=(1-\eta)^{-4}\{-(1+2\eta)^{2}+6\eta(1+0.5\eta)^{2}r^{*}-0.5\eta(1+2\eta)^{2}(r^{*})^{3}\},$$

$$r^{*}<1 \qquad (3.1.6)$$

where

$$\eta=\frac{1}{6}\pi\rho\sigma^{3} \qquad (3.1.7)$$

is the dimensionless packing density and $r^{*}=r\sigma^{-1}$ is the scaled distance. As a result of the discontinuity of the direct correlation function $c(r^{*})$, (3.1.4) and (3.1.5), at $r^{*}=1$ the radial distribution function $g_{\sigma}(r^{*})$ is piecewise analytic function and can be represented as:

$$g_{\sigma}(r^{*})=\sum_{n=0}^{\infty}H(r^{*}-n)g_{n}(r^{*}) \qquad (3.1.8)$$

where H(x) is the Heaviside step function.

The W-T radial distribution function is continous exept at $r^*=1$ and hence, for $n\neq 1$, $g_n(n)=0$. From (3.1.4) follows that $g_0(r^*)=0$. The analytic expression for $g_1(r^*)$ was given by Wertheim (1963) and Thiele (1963) and for $g_i(r^*)$, $i=2,3,4$ by Smith and Henderson (1970). It was also demonstrated that for $r^*>5$ $g(r^*)$ can be well approximated by unity. In the interval $1<r^*<2$ the W-T radial distribution function is given by:

$$g_\sigma(r^*)=(r^*)^{-1}(1-\eta)^{-2}\sum_{k=0}^{2} A_k \exp\{t_k(r^*-1)\} \qquad (3.1.9)$$

where

$$A_k=3^{-1}\sum_{m=0}^{2} H_m\, j^{mk},$$

and

$$H_0=1+\frac{1}{2}\eta,$$

$$H_1=-(4\eta)^{-1}(f^2+1/8)^{-1/2}[x_-^2(1-3\eta-4\eta^2)+x_+(1-(5/2)\eta^2)],$$

$$H_2=(4\eta)^{-1}(f^2+1/8)^{-1/2}[x_+^2(1-3\eta-4\eta^2)+x_-(1-(5/2)\eta^2)],$$

One also has, for $k=0,1,2$

$$t_k=2\eta(1-\eta)^{-1}[-1+x_+j^k+x_-j^{-k}],$$

$$j=\exp\{\frac{2}{3}\pi i\}$$

$$x_\pm=\pm[\pm f+(f^2+1/8)^{1/2}]^{1/3}$$

and

$$f=(4\eta^2)^{-1}(3+3\eta-\eta^2)$$

The Fourier transform of the direct correlation function (3.1.5) applied in Eq.(2.3.14) gives the structure factor of the hard sphere fluid. Ashcroft and Lekner (1966) used this method in their study on the structure and resistivity of liquid metals. They treated the packing density η as an adjustable parameter. An agreement of their results and the experimental structure factor in the region of the major peak was observed for $\eta \approx 0.45$ but was not satisfactory beyond that region.

3.2 THE METHOD OF WEEKS, CHANDLER AND ANDERSEN (WCA)

It is a well accepted notion of liquid state theory that the effective pair potential $\psi(r)$ (see Eq.2.3.1) consists. irrespective of details, of a quickly decaying, repulsive part. decreasing to the principal minimum which occurs at $r=r_0$ and a long range tail representing the attraction.

Weeks, Chandler and Andersen (1971) proposed the separation of the potential into 'soft core' repulsive part:

$$\psi_0(r)= \begin{cases} \psi(r)-\psi(r_0) & (r<r_0) \\ 0 & (r>r_0) \end{cases} \tag{3.2.1}$$

and the 'tail'-remainder of the interaction:

$$\psi_1(r)= \begin{cases} \psi(r_0) & (r<r_0) \\ \psi(r) & (r>r_0) \end{cases} \tag{3.2.2}$$

WCA used the Lennard-Jones ('12-6') model potential in their study, but the general expression (3.2.1)-(3.2.2) is sufficient for further discussion and still valid for realistic liquid metals potentials (Chapter 5).

Following the van de Waals idea, WCA treat the repulsive part of the potential, $\psi_0(r)$ as a dominant part responsible for the quantitative behavior of the liquid structure factor at intermediate and large wave vectors. The contribution of a 'tail' is treated as a perturbation of a particular importance only in the small wave vector part of the structure factor.

We define the 'soft sphere' reference fluid as the one described by the repulsive part of the potential $\psi_0(r)$.

One introduces the Boltzmann factors for hard (e_σ) and soft (e) sphere fluid by the equations:

$$e_\sigma(r)=\exp\{-\beta\psi_\sigma(r)\} \qquad (3.2.3)$$

$$e(r)=\exp\{-\beta\psi_0(r)\} \qquad (3.2.4)$$

where ψ_σ and ψ_0 are given by Eqs.(3.1.3) and (3.2.1) respectively.

We observe that, if the hard core diameter σ is chosen properly, the function $\Delta e(r)=e(r)-e_\sigma(r)$ takes non-zero values in a very narrow range of arguments centered around $r=\sigma$. The recipe for finding the optimum hard core diameter σ is given within the framework of the blip-function theory (see for example Andersen *et al.*,1971,1976).

The excess Helmholtz free energy A_{ex} for a system of particles described by a Hamiltonian (2.1.8) is given by:

$$A_{ex}= -\beta^{-1}\ln Q \qquad (3.2.5)$$

where Q is the configurational integral defined by Eq.(2.1.16). When the external potential is not applied (V=0 in Eq.2.1.16) then one writes a functional Taylor expansion of the dimensionless excess Helmholtz free energy density $A=-\beta A_{ex}/V$ in powers of $\Delta e(r)$:

$$A(\beta,\rho;e)=A(\rho;e_\sigma)+\int d\underline{r}\frac{\delta A(\rho;e_\sigma)}{\delta e_\sigma(r)}\Delta e(r)$$

$$+ \text{ higher order terms} \qquad (3.2.6)$$

We employ the result (Hansen and MacDonald,1976):

$$\frac{\delta A}{\delta e(r)} = \frac{1}{2}\rho^2 \tau(r) \tag{3.2.7}$$

where $\tau(r)=\exp\{\beta\psi(r)\}g(r)$, and then Eq.(3.2.6) becomes:

$$A-A_\sigma = \frac{1}{2}\rho^2 \int d\underline{r}\,\tau_\sigma(r)\Delta e(r)+\ldots \tag{3.2.8}$$

where $A_\sigma=A(\rho;e_\sigma)$ and $\tau_\sigma(r)$ is given by Eq.(3.1.5).

In order to minimize the difference on the LHS of the above equation WCA naturally require the fulfilment of the condition:

$$\int d\underline{r}B_\sigma(r)= 0 \tag{3.2.9}$$

where $B_\sigma(r)$ is called the 'blip function' and is given by:

$$B_\sigma(r)=\tau_\sigma(r)\Delta e(r) \tag{3.2.10}$$

We define the Fourier transform of the 'blip function':

$$\hat{B}(k)=\int d\underline{r}B_\sigma(r)\exp\{i\underline{k}\cdot\underline{r}\} \tag{3.2.11}$$

and now the condition (3.2.9) for the best temperature- and density-dependent hard sphere diameter σ associated with the soft sphere system with the potential ψ_0, is rewritten:

$$\hat{B}(0)= 0 \tag{3.2.12}$$

It was proven (Andersen *et al.*,1971) that in terms of the softness parameter ξ:

$$\xi=\sigma^{-1}\int_0^\infty dr\,|B_\sigma(r)| \tag{3.2.13}$$

which, for harshly repulsive potentials is much less than unity, the expressions (3.2.8) and (3.2.9) give:

$$A=A_\sigma+O(\xi^4) \tag{3.2.14}$$

The formula (3.2.14) serves as a prescription for studying the thermodynamical properties of the soft sphere fluid. In order to study the structure one has to find an expression for the radial distribution function. We notice that from Eqs.(3.2.7), (3.2.8) and (3.2.9) follows the result:

$$\tau(r)=\tau_{\sigma}(r) + \text{higher order terms} \qquad (3.2.15)$$

And from the definition of the function $\tau(r)$ (see comment below Eq.(3.2.7)) one obtains the radial distribution function in the WCA approximation

$$g_{WCA}(r)=\exp\{-\beta\psi_{0}(r))\}\tau_{\sigma}(r)[1+O(\xi^{2})] \qquad (3.2.16)$$

Combining Eqs.(3.2.9), (3.2.15) and (3.2.16) yields an important relation between the structure factors of the WCA reference fluid and the corresponding hard sphere fluid in k=0 limit:

$$S_{WCA}(0) = S_{HS}(0;\eta) \qquad (3.2.17)$$

Physically, the above expression states the requirement of equal isothermal compressibilities of the WCA soft sphere and the hard sphere fluid (see Eq.(2.3.13)).

Inspection of the formulas (3.2.14) and (3.2.16) suggests that the thermodynamic functions will be better approximated within the WCA theory than the structure. From Eq.(3.2.16) one easily obtains:

$$h(r)=h_{\sigma}(r)+B(r) \qquad (3.2.18)$$

where $h(r)$ is the total correlation function given by (2.1.27).

Now we apply the expression (2.3.11) and this yields the crudest form of the structure factor in WCA theory:

$$S_{WCA}(k) = S_{\sigma}(k)+\rho\hat{B}(k) \qquad (3.2.19)$$

This formula is not appropriate for potentials which are softer than the repulsive part of a typical Lennard-Jones potential, as is the case for liquid metals (Kumaravadivel and Evans, 1976).

Jacobs and Andersen (1975) point out that the spurious peak at $k \approx \pi/\sigma$ in the liquid metal structure factor is caused by the presence of the extremas in $\hat{B}(k)$ at multiples of π/σ. They present a more accurate approximation which is obtained within the diagramatic summation method. After topological reduction of the bonds in a diagramatic representation of the total correlation function h(r), they sum only selected terms of the expansion which give non-negligible contribution. This procedure yields the approximate expression for the structure factor of the reference soft sphere fluid which (denoted by S_0), was adopted in the present study, (another derivation can be found in Telo Da Gama and Evans, 1980):

$$S_0(k) = S_{\sigma}(k)\{1-\rho\hat{B}(k)S_{\sigma}(k)\}^{-1} \qquad (3.2.20)$$

In order to calculate $S_0(k)$ we only need to know the radial distribution function for the hard sphere fluid. The Wertheim-Thiele solution for $g_{\sigma}(r)$ (Eq.3.1.9) did not prove to be accurate enough for this kind of calculation. Verlet and Weis (1972) derived an analytical expression for the radial distribution function of the hard sphere fluid based on the W-T solution.

Their result fits the 'exact' computer experiment values very well and we used it in the course of our calculations. We denote all functions and parameters introduced by Verlet and Weis by a subscript $_{VW}$ and that due to Wertheim–Thiele by a subscript $_{\sigma}$.

Verlet and Weis postulate that:

$$g_{VW}(r/\sigma_{VW},\eta_{VW})=g_{\sigma}(r/\sigma,\eta)+\delta g_1(r) \qquad (3.2.21)$$

where the following relation holds:

$$\eta=\eta_{VW}-\frac{1}{16}\eta_{VW}^{2} \qquad (3.2.22)$$

$\delta g_1(r)$ is a short range term defined by:

$$\delta g_1(r)=(A/r)\exp\{-\mu(r-\sigma_{VW})\}\cos\mu(r-\sigma_{VW}) \qquad (3.2.23)$$

By inserting $r=\sigma_{VW}$ in Eq.(3.2.21) and with a help of the empirical equation of state for hard spheres due to Carnahan and Starling (1969) one obtains the expression for calculating the parameter A:

$$\frac{A}{\sigma_{VW}}=\frac{3}{4}\,\eta^{2}(1-0.7117\eta-0.114\eta^{2})(1-\eta)^{-4} \qquad (3.2.24)$$

The parameter μ is found from the demand that the hard sphere fluid compressibilities calculated using the Carnahan and Starling equation of state and the W-T approximation be the same at the transition point. This yields:

$$\mu\sigma_{VW}\simeq\frac{24(A/\sigma_{VW})}{\eta g_{\sigma}(1,\eta)}=\frac{24(A/\sigma_{VW})}{\eta}(1-\eta)^{2}(1+\frac{1}{2}\eta)^{-1} \qquad (3.2.25)$$

Now, with the corrected radial distribution function the formula (3.2.20) is written:

$$S_0(k) = S_{VW}(k)\{1-\rho\hat{B}_{VW}(k)S_{VW}(k)\}^{-1} \qquad (3.2.26)$$

CHAPTER 4

THE LOW ANGLE STRUCTURE FACTOR THEORY

In Chapter 3 the structure factor of the reference fluid of soft spheres, determined by the repulsive part of the effective pair-potential (3.2.1) has been derived. The expression (3.2.26) gives accurate numerical results for higher angles of scatter (Jacobs and Andersen,1975; Meyer *et al.*,1980,1981; McLaughlin and Young,1982a). The potential tail (3.2.2) manifests its importance in a low-$\underline{k}$ region of the structure factor (Henderson and Ashcroft,1976; McLaughlin and Young,1981,1982b). The various theoretical approaches which aim at explaining the long wavelength range of the liquid structure factor are presented in this chapter.

4.1 THE RANDOM PHASE APPROXIMATION (RPA), THE MEAN DENSITY APPROXIMATION (MDA) AND THE EXTENDED RANDOM PHASE APPROXIMATION (ERPA).

The first attempt to incorporate the effects of the potential tail on the small-angle structure factor in dense fluids was made, using the random phase approximation (RPA), by Woodhead-Galloway *et al* in 1968. In their study on the structure of binary mixtures Henderson and Ashcroft (1976) derived the mean density approximation (MDA) which was superior to RPA. Evans and Schirmacher (1978) obtained the extended random phase approximation (ERPA) as a special case of MDA. We present the derivation of the above three approximations within the framework of the statistical mechanics of non-uniform, classical fluids (Evans,1979).

Let us use the result (McDonald and O'Gorman, 1978, p.81):

$$\rho^{(2)}(\underline{r}_1,\underline{r}_2)= 2\frac{\delta\Omega_V[\rho_0]}{\delta\psi(\underline{r}_1,\underline{r}_2)} \qquad (4.1.1)$$

where $\Omega_V[\rho_0]$ is the grand thermodynamic potential given by Eqs.(2.2.6) and (2.2.8) and $\psi(\underline{r}_1,\underline{r}_2)$ is the pair-wise potential given by Eq.(2.3.1) in a case of the non-uniform fluid. From the above formula and Eqs.(2.2.6) and (2.2.12) one obtains:

$$\rho^{(2)}(\underline{r}_1,\underline{r}_2)= 2\frac{\delta F[\rho_0]}{\delta\psi(\underline{r}_1,\underline{r}_2)} \qquad (4.1.2)$$

where the intrinsic Helmholtz free energy $F[\rho]$ is defined by Eq.(2.2.5). We chose the parametrization of the potential $\psi(\underline{r}_1,\underline{r}_2)$ in the following way:

$$\psi_\mu \equiv \psi(\underline{r}_1,\underline{r}_2;\mu)=\psi_0(\underline{r}_1,\underline{r}_2) + \mu\psi_1(\underline{r}_1,\underline{r}_2) \qquad (4.1.3)$$

where the terms ψ_0 and ψ_1 are defined by Eqs.(3.2.1) and (3.2.2) respectively and are appropriate for non-uniform fluids. The parameter $0\leqslant\mu\leqslant1$ switches on ($\mu\neq0$) and off ($\mu=0$) the long-range effects. Now the functional integration of the expression (4.1.2) along a one-parameter integration path (4.1.3) yields:

$$F[\rho_0]-F_0[\rho_0]=\int_0^1 d\mu\int d\underline{r}_1 d\underline{r}_2 \frac{\delta F[\rho_0]}{\delta\psi_\mu(\underline{r}_1,\underline{r}_2)}\,\frac{d\psi_\mu(\underline{r}_1,\underline{r}_2)}{d\mu} \qquad (4.1.4)$$

where $F_0[\rho_0]$ corresponds to the reference system. This formula, with a help of the results (4.1.2) and (4.1.3) gives:

$$F[\rho_0]=F_0[\rho_0]+ 1/2\int_0^1 d\mu\int d\underline{r}_1 d\underline{r}_2\rho^{(2)}(\psi_\mu;\underline{r}_1,\underline{r}_2)\psi_1(\underline{r}_1,\underline{r}_2) \qquad (4.1.5)$$

From Eqs.(2.2.10),(2.2.14) and (2.2.16) it follows that:

$$\beta\frac{\delta^2 F[\rho]}{\delta\rho(\underline{r})\delta\rho(\underline{r}')} = \delta(\underline{r}-\underline{r}')\frac{1}{\rho(\underline{r})} - c[\rho;\underline{r},\underline{r}'] \qquad (4.1.6)$$

One applies the operator $\frac{\delta^2}{\delta\rho(\underline{r})\delta\rho\underline{r}')}$ on both sides of Eq.(4.1.5) and in a case of a fluid in which the interaction potential is central this yields:

$$c^{(2)}(r_{12})-c_0^{(2)}(r_{12}) = -\frac{\beta}{2}\frac{\delta^2}{\delta\rho(\underline{r}_1)\delta\rho(\underline{r}_2)}\int_0^1 d\mu\int d\underline{r}_1 d\underline{r}_2\rho^{(2)}(\mu;\underline{r}_1,\underline{r}_2)\psi_1(r_{12}) \qquad (4.1.7)$$

In order to progress any further it is necessary to evaluate $\rho^{(2)}(\mu;\underline{r}_1,\underline{r}_2)$. The random phase approximation (RPA) is easily obtained if all correlations between the particles are ignored and we put:

$$\rho^{(2)}(\mu;\underline{r}_1,\underline{r}_2)=\rho(\underline{r}_1)\rho(\underline{r}_2) \qquad (4.1.8)$$

From this, Eqs.(4.1.7) and (2.3.14) it follows that in RPA the structure factor is expressed by the formula:

$$S_{RPA}(k) = S_0(k)\{1+\beta\rho S_0(k)\psi_1(k)\}^{-1} \qquad (4.1.9)$$

where $S_0(k)$ is the structure factor of the reference system (Eq.(3.2.26)) and $\psi_1(k)$ is the Fourier transform of the potential tail.

One can simplify the calculations by expanding the integrand in Eq.(4.1.7) in terms of the two-body distribution function of the reference, non-uniform fluid $\rho^{(2)}(\mu=0;\underline{r}_1,\underline{r}_2)=\rho^{(2)}(\underline{r}_1,\underline{r}_2)$.

The integral in (4.1.7) is than written:

$$\mathcal{J}= \int d\underline{r}_1 d\underline{r}_2\rho^{(2)}(\underline{r}_1,\underline{r}_2)\psi_1(r_{12}) \qquad (4.1.10)$$

Let us assume that the fluid is weakly non-uniform. The configurational two-body distribution function can be evaluated at the mean local density (Henderson and Ashcroft,1976) and this is written:

$$\rho_o^{(2)}(\underline{r}_1,\underline{r}_2)=\rho_o^{(2)}(r_{12})+1/2\{\delta\rho(\underline{r}_1)+\delta\rho(\underline{r}_2)\}\frac{\partial\rho_o^{(2)}(r)}{\partial\rho} + 1/2\ \delta\rho(\underline{r}_1)\delta\rho(\underline{r}_2)\frac{\partial^2\rho_o^{(2)}(r)}{\partial\rho^2} + \ldots \qquad (4.1.11)$$

This approximation was named the mean-density approximation (MDA). Applying it in Eq.(4.1.7) leads to the result:

$$c^{(2)}(r)-c_o^{(2)}(r) = -(\beta/2)\psi_1(r)\frac{\partial^2\rho^{(2)}(r)}{\partial\rho^2} \qquad (4.1.12)$$

After Fourier transforming, this becomes:

$$c^{(2)}(k)-c_0^{(2)}(k) = -\frac{\beta}{2(2\pi)^3}\int d\underline{q}\,\psi_1(q)\frac{\partial^2}{\partial\rho^2}\rho_o^{(2)}(|\underline{k}-\underline{q}|) \qquad (4.1.13)$$

It is easy to check that:

$$\rho^{(2)}(k)=(2\pi)^3\rho^2\delta(k) + \rho\{S(k)-1\} \qquad (4.1.14)$$

where one uses Eqs.(2.3.10) and (2.1.24).

From (4.1.13), (4.1.14) and (2.3.14) it follows that:

$$S_{MDA}^{-1}(k) = S_0^{-1}(k) + \beta\rho\psi_1(k) + \beta\rho(2\pi)^{-3}\int d\underline{q}\,\psi_1(q)\{\frac{\partial}{\partial\rho}S_0(|\underline{q}-\underline{k}|)+(\rho/2)\frac{\partial^2}{\partial\rho^2}S_0(|\underline{q}-\underline{k}|)\} \qquad (4.1.15)$$

As was noted by many authors (Henderson and Ashcroft,1976; Evans and Schirmacher,1978) the above relation, also called the mean-density approximation (MDA) can be valid only at small wave vectors because the expansion (4.1.11) assumes slow and small variations of the density $\rho(\underline{r})$ about the mean value.

At the k=0 limit the MDA result is exact to first order in ψ_1 (see 4.1.10) and can be derived in the theory of uniform fluids using the compressibility sum rule and the coupling constant algorithm for free energies per atom of a homogeneous fluid (Evans and Schirmacher,1978).

The calculations of the structure factor using the MDA for Al, Mg, Na and Pb near melting were reported by McLaughlin and Young (1982a). For metals with resonably hard-core like repulsive part of the potential (Al, Mg) they obtained satisfactory results for both high and low argument range. They suggested, that in the case of Na and Pb the discrepances between MDA results and the experimental values at low-k region result from the softness of the potential (Na) and the importance of many-ion and density-dependent forces in this region (Pb).

One can obtain a simpler result than (4.1.15) if the density dependence of the radial distribution function g(r) in (4.1.12) is neglected. This yields:

$$c^{(2)}(r)-c_0^{(2)}(r) = -(\beta/2)\psi_1(r)g_0(r) \tag{4.1.16}$$

and Fourier transformation leads to the formula:

$$S_{ERPA}(k)=S_0(k)\{1+S_0(k)[\beta\rho\psi_1(k)+\frac{\beta}{(2\pi)}\int d\underline{q}\,\psi_1(q)(S_0(|\underline{q}-\underline{k}|)-1)]\}^{-1} \tag{4.1.17}$$

This result, named the ERPA-extended random phase approximation was obtained by Evans and Schirmacher (1978).

4.2 THE GASKELL'S APROXIMATION (GA)

We present yet another approximation for the long-wavelength limit of the structure factor, which was originally derived by Gaskell in 1978. We show that Gaskell's approximation is a member of the hierarchy of approximations based on the MacLaurin expansions of the structure factor in terms of the perturbing 'tail' of the potential.

Let us recall the definition of the structure factor:

$$S(k) = N^{-1}\langle \rho_{\underline{k}}\rho_{-\underline{k}}\rangle \quad , \underline{k}\neq 0 \qquad (2.3.7a)$$

where $\rho_{\underline{k}}$ is the particle density in $\underline{k}$-space defined by Eq.(2.3.6). One utilizes the parametrization of the potential in terms of switch on/off parameter $0\leqslant\mu\leqslant 1$ introduced by Eq.(4.1.3). The potential energy arising from $\psi_1(r)$ is represented in terms of the density fluctuations:

$$U_{\psi} = (2N)^{-1}\sum_{\underline{q}}\psi_1(q)\rho_{\underline{q}}\rho_{-\underline{q}} \qquad (4.2.1)$$

Now the parametrized structure factor can be written:

$$S_{\mu}(k)=N^{-1}\frac{\int\prod_i d\underline{r}_i\rho_k\rho_{-k}\exp(-\beta H_0-\frac{\mu\beta}{2N}\sum_q\psi_1(q)\rho_{\underline{q}}\rho_{-\underline{q}}\}}{\int\prod_i d\underline{r}_i\exp(-H_0-\frac{\mu\beta}{2N}\sum_q\psi_1(q)\rho_{\underline{q}}\rho_{-\underline{q}}\}} \qquad (4.2.2)$$

where H_0 is a soft sphere system Hamiltonian.

$S_{\mu=1}(k)$ can be found by using MacLaurin expansions of different orders. In general, for a function $f(\mu)$, ordinary MacLaurin expansion including remainder term is written:

$$f(\mu=1)=\sum_{S=0}^{n-1}(s!)^{-1}\left.\frac{\partial^s f(\mu)}{\partial\mu^s}\right|_{\mu=0} + \int_0^1 d\mu\frac{\partial^n f(\mu)}{\partial\mu^n}\frac{(1-\mu)^{n-1}}{(n-1)!} \qquad (4.2.3)$$

Let us consider three cases when n=1,2,3 and $f(\mu)=S_{\mu}^{-1}(k)$. We expand the reciprocal of the structure factor because it has an immediate connection with the short ranged direct correlation function (2.3.14).

For n=1 we obtain the commonly used coupling parameter formula:

$$S^{-1}(k) = S_{0}^{-1}(k) + \int d\mu \frac{\partial}{\partial\mu} S_{\mu}^{-1}(k) \qquad (4.2.4)$$

where $S_0(k)$ is the structure factor of the soft sphere reference fluid.

In order to calculate the complicated integral on the RHS of the above expression Gaskell expands the integrand about $\mu=0$ and neglects all terms exept the zeroth (independent of μ) one (Gaskell,1961;1978). But this is equivalent to taking the MacLaurin expansion for n=2 and neglecting the remainder, integral term in (4.2.3). This way we arrive to the result:

$$S^{-1}(k) = S_{0}^{-1}(k) + \frac{\partial}{\partial\mu} S_{\mu}^{-1}(k) \qquad (4.2.5)$$

which can be rewritten as follows:

$$S(k) = S_0(k)\{1-S_0^{-1}(k)\frac{\partial}{\partial\mu} S_{\mu}(k)\Big|_{\mu=0}\}^{-1} \qquad (4.2.6)$$

Now our task is to calculate the partial derivative of the structure factor appearing in the above formula. To end this we write:

$$S_{\mu}(k) = N^{-1} \frac{L_{\mu}}{Z_{\mu}} \qquad (4.2.7)$$

where the numerator L_{μ} and the denominator Z_{μ} are given explicitely by Eq.(4.2.2).

Z_μ obviously represents the partition function of the canonical ensemble with a Hamiltonian $H_0+\mu U_\psi$. With a help of this shorthand notation we have:

$$\frac{\partial}{\partial\mu}S_\mu(k) = N^{-1}\{Z_\mu^{-1}\frac{\partial}{\partial\mu}L_\mu(k) - \frac{L_\mu(k)}{Z_\mu}\frac{\partial}{\partial\mu}Z_\mu\} \tag{4.2.8}$$

and after differentiation we obtain:

$$\begin{aligned}\frac{\partial}{\partial\mu}S_\mu(k) = -\frac{\beta}{2N^2}Z_\mu^{-1}\sum_q\psi_1(q)\int\prod_i d\underline{r}_i\,|\rho_{\underline{q}}|^2|\rho_{\underline{k}}|^2\exp\{-\beta(H_0+\mu U_\psi)\}\\ + N^{-2}\frac{L_\mu(k)}{Z_\mu}(\beta/2)\sum_q\psi_1(q)L_\mu(q)\end{aligned} \tag{4.2.9}$$

This, again, may be simply written as:

$$\begin{aligned}\frac{\partial}{\partial\mu}S_\mu(k) = -(\beta/2)\sum_q\psi_1(q)\langle N^{-2}|\rho_{\underline{k}}|^2|\rho_{\underline{q}}|^2\rangle_\mu\\ +(\beta/2)\sum_q\psi_1(q)\langle N^{-1}|\rho_{\underline{k}}|^2\rangle_\mu\langle N^{-1}|\rho_{\underline{q}}|^2\rangle_\mu\end{aligned} \tag{4.2.10}$$

We notice, that each sum in this expression can be split into two terms involving $\underline{q}=\pm\underline{k}$ and the remaining sum over $\underline{q}\neq\pm\underline{k}$, and (4.2.10) is finally rewritten as:

$$\begin{aligned}\frac{\partial}{\partial\mu}S_\mu(k)\Big|_{\mu=0} = \beta\psi_1(k)\{\langle N^{-1}|\rho_{\underline{k}}|^2\rangle_0^2 - \langle N^{-2}|\rho_{\underline{k}}|^4\rangle_0\}\\ +(\beta/2)\sum_{q\neq\pm k}\psi_1(q)\{\langle N^{-1}|\rho_{\underline{k}}|^2\rangle_0\langle N^{-1}|\rho_{\underline{q}}|^2\rangle_0 - \langle N^{-2}|\rho_{\underline{k}}|^2|\rho_{\underline{q}}|^2\rangle_0\}\end{aligned} \tag{4.2.11}$$

At this point we need to know the following matrix elements:

$$\langle N^{-2}|\rho_{\underline{k}}|^4\rangle_0\ ,\ \underline{k}\neq 0 \tag{4.2.12}$$

and

$$\langle N^{-2}|\rho_{\underline{q}}|^2|\rho_{\underline{k}}|^2\rangle_0\quad ,\underline{k},\underline{q},\underline{k}\pm\underline{q}\neq 0 \tag{4.2.13}$$

The values of the above and similar expressions were calculated in the quantum theory of liquid helium (Feenberg,1969,1970) and also in a very general and elegant way by Wu (1971a,b). The latter method required the use of the convolution approximation for the n-body configurational distribution function (Wu and Chien,1970). It is argued, (Gaskell,1978), that dispite the fact that the convolution approximation produces distributions which are unsatisfactory for very small interparticle separations, it can be used in the present case where the distribution functions are integrated against the longe-range potential component only.

Without going into details of these calculations we only quote the results:

$$\langle N^{-2}|\rho_{\underline{k}}|^4\rangle_0 = 2S_0^{\,2}(k) + \mathcal{O}(N^{-1}) \;,\; \underline{k}\neq 0 \tag{4.2.12'}$$

and

$$\begin{aligned}\langle N^{-2}|\rho_{\underline{q}}|^2|\rho_{\underline{k}}|^2\rangle_0 &= S_0(q)S_0(k) + N^{-1}S_0^{\,2}(q)S_0^{\,2}(k)\\ &\times[S_0(|\underline{k}+\underline{q}|)+S_0(|\underline{k}-\underline{q}|)-2] \;, \qquad \underline{k},\underline{q},\underline{k}\pm\underline{q}\neq 0\end{aligned} \tag{4.2.13'}$$

We note at this point, that the formulas (4.2.12') and (4.2.13') also valid for $\mu\neq 0$, e.g. when we 'switch on' the perturbation-tail of the potential. Now Eq.(4.2.11) becomes:

$$\begin{aligned}\frac{\partial}{\partial\mu}S_\mu(k)\Big|_{\mu=0} &= -\beta\Psi_1(k)S_0^{\,2}(k) - \beta\sum_{\underline{q}\neq\pm\underline{k}}\Psi_1(q)\{N^{-1}S_0^{\,2}(k)S_0^{\,2}(q)\\ &\times[S_0(|\underline{k}+\underline{q}|)-1]\}\end{aligned} \tag{4.2.14}$$

We convert a sum into an integral:

$$\sum_{\underline{k}} \rightarrow \frac{V}{(2\pi)^3}\int d\underline{k} \tag{4.2.15}$$

And finally combining (4.2.14) and (4.2.6) yields the Gaskell's approximation (GA):

$$S(k) = S_0(k)\{1 + S_0(k)[\beta\rho\psi_1(k) + \frac{\beta}{(2\pi)^3}\int d\underline{q}\psi_1(q)S_0^{\,2}(q)(S_0(|\underline{k}+\underline{q}|)-1)]\}^{-1} \tag{4.2.16}$$

If we neglect the terms involving the coupling of density fluctuations of different wavenumbers in (4.2.11) than the result (4.2.16) reduces to the RPA given by Eq.(4.1.9). The correlation parts of GA and ERPA, represented by integral terms in Eqs.(4.1.17) and (4.2.16), are very similar, the only difference is the presence of $S_0^{\,2}$ factor in GA. The computed values of the structure factor for some liquid metals in GA and ERPA will be presented in Chapter 6.

We now return to the Gaskell initial expression (4.2.4). We combine Eq.(4.2.4) and (4.2.14) and it gives:

$$S(k) = S_0(k)\{1 + S_0(k)[\beta\rho\psi_1(k) + \beta\int_0^1 d\mu G(k,\mu)]\}^{-1} \tag{4.2.17}$$

where

$$G(k,\mu) = (2\pi)^{-3}\int d\underline{q}\psi_1(q)S_\mu^{\,2}(q)[S_\mu(|\underline{q}+\underline{k}|)-1] \tag{4.2.18}$$

Chakravarty and Woo (1976) have shown, that assuming that $G(k,\mu)$ is slowly varying function of μ and is also analytic than instead of expanding it about $\mu=0$ (Gaskell,1961) it can be expanded about $\mu=1$:

$$G(k,\mu) = G(k,1) + (\mu-1)\frac{\partial G(k,\mu)}{\partial \mu}\bigg|_{\mu=1} + \dots \tag{4.2.19}$$

Truncating this expansion at the first term leads to an approximate expression:

$$S(k)= S_0(k)\{1+ S_0(k)[\beta\rho\psi_1(k)+ \beta(2\pi)^{-3}\int d\underline{q}\psi_1(q)S^2(q)[S(|\underline{q}+\underline{k}|)-1]\}^{-1} \tag{4.2.20}$$

An integral equation of this type can in principle be solved numerically by iterative method (Chakravarty and Woo,1976). The initial equation to solve would be equation of the GA type (4.2.16).

Now we can examine the last choice of n=3 in MacLaurin expansion (4.2.3) which gives:

$$S^{-1}(k) = S_0^{-1}(k) + \frac{\partial}{\partial\mu}S_\mu^{-1}(k)\Big|_{\mu=0} + \frac{\partial^2}{\partial\mu^2}S_\mu^{-1}(k)\Big|_{\mu=0} + R \tag{4.2.21}$$

Again we neglect the remainder term R. The second order partial derivative of the structure factor involves the higher order density correlation functions. Its full form is presented in Appendix A.

CHAPTER 5

THE PAIR POTENTIAL FOR SIMPLE LIQUID METALS

In the previous chapters we developed the general theory of the structure factor for a classical, one-component liquid. We did not specify any particular physical system. The only requirement we imposed on the potential was that it had to be pair-wise and additive, Eq.(2.3.1). We now turn to study the specific case of the simple liquid metals.

Liquid metals are viewed as systems composed of two intermingled fluids: the conduction valence electron gas and positively charged massive ions. Liquid metals have resistivities in the range 10-100μohm·cm and often a positive temperature coefficient of resistivity (Ashcroft and Stroud,1978). Simple liquid metals form a subgroup of liquid metals and are characterised by two-particle and central interactions. Although liquid metals consist of two types of particles: electrons and ions and there are three types of two-body interactions (ion-ion, electron-electron and electron-ion), we can still apply the formalism developed earlier for one component dense fluid. In doing so we reduce the liquid metal to a quasi-one component fluid characterised by the effective pair potential developed between the pairs of ions. We can separate this effective pair potential according to WCA prescription (3.2.1)-(3.2.2) and calculate the ionic static structure factor for simple liquid metals.

The method of obtaining the effective pair potential for liquid metals is well established and widely accepted (Ashcroft and Stroud,1978; Kumaravadivel and Evans,1976; Dharma-wardana and Aers,1983; McLaughlin and Young,1982a).

In our exposition of the subject we follow the discussion contained in Ashcroft and Stroud,(1978).

Let us write the full Hamiltonian for the liquid metal:

$$H=\sum_{i} \frac{p_i^2}{2m} + 1/2 \sum_{i\neq j} \frac{e^2}{|\underline{r}_i-\underline{r}_j|} + \sum_{l} \frac{P_l^2}{2M}$$
$$+ 1/2 \sum_{l\neq l'} \frac{Z^2 e^2}{|\underline{R}_l-\underline{r}_{l'}|} + \sum_{il} v^p(\underline{r}_i-\underline{R}_l) \qquad (5.1)$$

where one assumes that the liquid metal has a volume V and consists of N ions of valence Z and of NZ electrons; $\{\underline{r}_i\}$ and $\{\underline{R}_j\}$ denoting electronic and ionic positions, $\{\underline{p}_i\}$ and $\{\underline{P}_j\}$ the corresponding momenta, m and M masses. The second, fourth and fifth terms in (5.1) represent electron-electron, ion-ion and and ion-electron interactions respectively.

$v^p(r)$ is the Ashcroft empty core model (ECM) pseudopotential (Ashcroft,1966,1968):

$$v^p(r)= \begin{cases} -\frac{Ze^2}{r} & r>r_c \\ 0 & r<r_c \end{cases} \qquad (5.2)$$

its Fourier transform is

$$v^p(q) = - \frac{4\pi Z}{q} \cos(qr_c) \qquad (5.3)$$

where r_c is the empty core radius which is fitted empirically.

The basic idea of the pseudopotential method (Harrison,1966,1980; Heine,1970; Wiser and Greenfield,1971) is to replace the one-electron Schrodinger equation

$$(T+V)\Psi_i = E_i\Psi_i$$

with T being the kinetic energy and V the self-consistent potential seen by each electron, by

$$(T+\hat{V}^p)\Phi_k = E_k\Phi$$

where $\Phi_k=(1-\hat{P})\Psi_k$ is the pseudo wave function, Ψ_k is the wave function of the valence electron, $\hat{P}$ is the operator projecting any function onto the core states and $\hat{V}^p$ is the pseudopotential operator. The eigen-energy spectrum of valence electron states of both T+V and $T+\hat{V}^p$ are the same. The pseudopotential $\hat{V}^p$ is weaker (as proved by the concellation theorem) than V and does not have bound core states. This means that the core electrons are treated as rigidly attached to the nucleus and only valence electrons' degrees of freedom are explicitely taken into account.

It should be noted that the pseudopotential operator $\hat{V}^p(r)$ is not uniqely defined and in general it is spatially non-local and energy dependent.

We use particulary simple, local (V^p is a function of r instead of an operator), one-parameter model pseudopotential of Ashcroft (5.2) which proved to be useful in many applications (McLaughlin and Young,1982a,1984; Hafner and Heine,1983). The different forms of pseudopotential like the modified point model (MPIM), the local Heine-Abarenkov (LHA) and many others are also found in the literature (Kumaravadivel and Evans,1976; Wiser and Greenfield,1971;Dharma-wardana and Aers,1983; Tanaka,1980).

In order to avoid the divergence problem exhibited by systems with long-range interactions we rewrite Eq.(5.1) in a following way:

$$H = \sum_{i} \frac{p_i^2}{2m} + 1/2 \sum_{j\neq i} \frac{e^2}{|\underline{r}_i - \underline{r}_j|} - E' \tag{5.4a}$$

$$+ 1/2 \sum_{l\neq j} \frac{Z^2 e^2}{|\underline{R}_l - \underline{R}_j|} + E' + E'' \tag{5.4b}$$

$$+ \sum_{il} v^p(\underline{r}_i - \underline{R}_l) - E'' \tag{5.4c}$$

$$+ \sum_{l} \frac{p_l^2}{2M} \tag{5.4d}$$

where E' represents the self-energy of a uniform charge density $\rho_e|e|$, $(\rho_e = \frac{NZ}{V})$ and is written:

$$E' = 1/2 \int d\underline{r} \int d\underline{r}' \, \frac{(\rho_e e)^2}{|\underline{r} - \underline{r}'|} \tag{5.5}$$

and E" is the Coulomb interaction between the ions and an uniform negative background. E" is written:

$$E'' = 1/2 \sum_{l} \int d\underline{r} \, \frac{Ze^2 \rho}{|\underline{r} - \underline{R}_l|} \tag{5.6}$$

As was shown by Ashcroft and Stroud (1978) the Fourier transform of (5.4) is written:

$$H = H_{eg} + U_M + H'_{ei} + NE_0 + H_k \tag{5.7}$$

where H_{eg} is the Hamiltonian for an interacting electron gas embedded in a uniform positive background ((5.4a) in q-representation), U_M is the electrostatic energy of the charged point ions in a neutralizing background ((5.4b) in q-representation), H'_{ei} is the ion-electron interaction term, E_0-so called Hartree energy and H_k is the ionic kinetic energy. The first and the third terms only on the RHS of the above formula involve electronic degrees of freedom.

Without going into the details of the calculation we only quote here the most important steps which have been performed (Ashcroft and Stroud,1978) to obtain an effective potential energy of the liquid metal.

i) The Helmholtz free energy per ion for the canonical ensemble is:

$$F = -(\beta N)^{-1} \ln Z \tag{5.8}$$

here Z is the partition function given by Eq.(2.1.13) and we use the Hamiltonian (5.4).

Integration over momenta in the expression for Z and separation of the terms involving electronic degrees of freedom in the Hamiltonian yields:

$$Z = \left(\frac{2\pi M}{h}\right)^{3N/2}(N!)^{-1}\int \prod_i d\underline{R}_i \exp\{-\beta(U_M+NE_0)\}$$

$$\times[\mathrm{Tr}_{(elec)}\exp\{-\beta(H'_{ei}+H_{eg})\}] \tag{5.9}$$

The bracketed factor can be replaced by:

$$\mathrm{Tr}_{(elec)}\exp\{-\beta(H'_{ei}+H_{eg})\} = \exp\{-\beta N F'(\underline{R}_1,\ldots,\underline{R}_N)\} \tag{5.10}$$

where $F'(\underline{R}_1,\ldots\underline{R}_N)$ can be treated as the Helmholtz free energy per ion of an interacting electron gas placed in the external potential described by H'_{ei}.

ii) Using the fact that H'_{ei} is weak, one can apply a coupling-constant formula which will express F' in terms of the Helmholtz free energy per ion of a uniform electron gas, F_{eg}:

$$NF' = NF_{eg} + \int_0^1 \frac{d\lambda}{\lambda}\langle\lambda H'_{ei}\rangle_\lambda \tag{5.11}$$

iii) The above relation can be calculated with the aid of the linear-response theory and this yields:

$$NF' = NF_{eg} + 1/2\, \nu^{-1} \sum_{q \neq 0} \chi^{(1)}(q) |v^{p}(q)|^{2} \rho_{\underline{q}} \rho_{-\underline{q}} \qquad (5.12)$$

where $\rho_{\underline{q}}$ is the ionic density in $\underline{q}$-space defined by (2.3.6). $\chi^{(1)}(q)$ is the density-density linear response function and can be expressed in terms of the dielectric function, $\epsilon(q)$, as follows:

$$\chi^{(1)}(q) = \frac{q^{2}}{4\pi e^{2}} \left\{ \frac{1}{\epsilon(q)} - 1 \right\} \qquad (5.13)$$

The dielectric function is given by:

$$\epsilon(q) = 1 - \frac{V_{c}(q)\chi_{o}(q)}{1+V_{c}(q)\chi_{0}(q)G(q)} \qquad (5.14)$$

where $V_{c}(q)=\frac{4\pi e^{2}}{q}$, χ_{0} is the free electron density response function:

$$\chi_{0}(q) = -\frac{mk}{\pi^{2}\hbar} \left[1/2 + \frac{(1-y^{2})}{4y} \ln\left|\frac{1+y}{1-y}\right| \right] \quad , \; y=q/(2k_{F}) \qquad (5.15)$$

and G(q) incorporates exchange and correlation effects and is called the local field.

It should be pointed that there exists a whole range of different models for the local field ,G(q), for example the density functional local-density approximation, the Geldart-Taylor model or Ichimaru-Utsumi model, (Dharma-wardana and Aers,1983). We use in our study a well accepted form due to Vashishta and Singwi (1972), which is written:

$$G(q) = A\,[1-\exp\{-4By^{2}\}] \qquad (5.16)$$

where y is defined by Eq.(5.15) and the parameters A and B for different densities are tabulated in (Vashishta and Singwi,1972).

With the results (5.9)-(5.16) we arrive at the expression for an effective potential energy function, U, for ions, with no explicit dependance on electronic degrees of freedom. The function U can be written in real space as a sum:

$$U(\underline{R}_1,\ldots,\underline{R}_N) = U_0(\rho) + 1/2 \sum_{l \neq j} \psi(\underline{R}_l - \underline{R}_j;\rho) \tag{5.17}$$

where $U_0(\rho)$ does not involve ionic coordinates and depends on the density of liquid. $\psi(R,\rho)$ is an effective pairwise ion-ion potential. Its Fourier transform is finally written (in atomic units):

$$\psi(q) = \frac{4\pi Z^2}{q} \{1 - F_N(q)\} \tag{5.18}$$

where the function $F_N(q)$ is the normalised energy-wave number characteristic expressed by:

$$F_N(q) = \left(\frac{V^p(q)q^2}{4\pi Z}\right)^2 \{1 - \epsilon(q)\} \tag{5.19}$$

In actual calculations described in Chapters 3 and 4 we required the effective pair potential in real space $\psi(r)$. The relation is given by the Fourier transform:

$$\psi(r) = (2\pi)^{-3} \int d\underline{q}\ \psi(q) \exp\{-i\underline{q}\cdot\underline{r}\} \tag{5.20}$$

The typical form of this potential for metals consists of the repulsive part $\psi_0(r)$ (see Eq.(3.2.1)) rapidly decreasing from $\psi(0)=\infty$ to its minimum value for $r=r_0$ (see Table II, column 3 and 4) and the oscillatory attracting 'tail' ψ_1. The oscillations are called Friedel oscillations and arise from the Fourier transformation of the logarithmic term in $\epsilon(q)$; this term exhibits a singularity at $q=2k_F$.

The tail of the potential $\psi_1(r)$ obtained according to WCA separation description (3.2.1)-(3.2.2) is shown in Fig.1 in the case of Aluminium, T=978K. The Fourier transform of the tail $\psi_1(q)$ which enters the formulae (4.1.17)-ERPA and (4.2.20)-GA is presented for the same case of Aluminium in Fig.2. The practical method of calculating $\psi_1(q)$ which avoids taking the Fourier transform for the second time (back to q-space) is sketched in Appendix B. We use this method because the Friedel oscillations are long range and relatively small and hence are very sensitive to the numerical procedure applied (for example Fast Fourier Transform); the other method (Appendix B) provides an appriopriate calculational tool for handling this sensitive problem.

CHAPTER 6

THE RESULTS OF NUMERICAL CALCULATIONS AND DISCUSSION

In this final chapter the results of calculation of the low-k region structure factor for three liquid metals at various temperatures obtained using Extended Random Phase Approximation (ERPA) and Gaskell's Approximation (GA) will be presented.

6.1 THE RESULTS OF CALCULATIONS

The theory of the structure factor for liquid metals which forms the basis of our calculations was presented in the previous chapters. We used expressions (3.2.20), (4.1.9), (4.1.17) and (4.2.16) in order to obtain the soft sphere reference system, RPA, ERPA and GA structure factor, respectively. This has been calculated for Rubidium (T=1900K, 350K, 313K), Aluminium (T=1330K, 978K, 943K) and Lead (T=613K). We used the effective pair potentials derived from pseudopotential theory as was discussed in Chapter 5. The relevant input data for all cases studied are contained in Table I. An example of the typical, long range part of the effective pair potential $\psi_1(r)$ (Eq.3.2.2) obtained from expressions (5.18)-(5.20) with Vashista and Singwi (1972) local field (5.16) for Aluminium at T=978K is shown in Fig.1. Its Fourier transform calculated from expressions (B.2) and (B.3) is presented in Fig.2. The values of the principal minimum of the effective pair potentials and their positions on the r-axis, as well as the hard core diameters obtained from 'blip' function theory are presented in Table II.

For each case studied we present two Figures (a and b). The first one (a) represents the comparison of the WCA-Jacobs and Andersen-Verlet and Weis soft sphere reference fluid structure factor $S_0(k)$, (3.2.20), the RPA result $S_{RPA}(k)$,(4.1.9) and the experimental values (where possible). The second one, (b), shows the results for RPA, ERPA and Gaskell's Approximation. It is important to notice the difference in scale of the k-axis in figures (a) and (b). The whole range of k-values in figure (b) is contained within the first two units of figure (a). One observes that the correlation corrections to RPA included in ERPA and GA are very small. We will discuss these effects shortly.

For Rubidium at T=1900K two different values of the Ashcroft empty core diameter, R_c, were used (see column 8, Table I). For the lower value of $R_c=2.45$, (Fig.3a), the RPA results give too high structure factor $S_{RPA}(k=0)=7.43$, whereas the value obtained by Franz *et al*.(1980), by linearly extrapolating the experimental results yields: $S_{exp}(k=0)=1.95$. The experimental error in their measurement was about ±15%. They also present the value calculated according to the Ornstein-Zernike relation from pVT-data, $S_{pVT}(k=0)=1.78$. For $R_c=2.60$ (Fig.4a) we obtain a realistic result , $S_{RPA}(k=0)=1.503$, which is comparable with the experimental values of Franz *et al*.(1980), (see above). McLaughlin and Young (1984a, b) calculated RPA and MDA theoretical values. Our result (Fig.4a) can be compared with their results which are in good agreement with experiment and represent noticeable improvement in this sensitive region, (Fig.3-McL&Y,1984b and Fig.3, Fig.7- McL&Y,1984a).

On the other hand Fig.4b shows no essential changes of the RPA result introduced by ERPA and GA. One notices that Gaskell's correction is even smaller in this case than the ERPA correction (see also Fig.3b-R_c=2.45).

In Fig.5a and b we again observe very small positive contribution of the GA correction to RPA for Rb, T=350K. This time the ERPA correction can not even be distinguished from the RPA (Fig.5b). The last studied case of Rubidium (Fig.6a, b) near melting, T=313K provides further confirmation of this situation.

The RPA produces higher values than WCA for k less than ≈7.5 A^{-1} in all studied cases for Rubidium. For T=350K and 313K the GA correction increases further the values of the structure factor whereas the ERPA correction is unnoticeable.

In Fig.7a and b the results for Aluminium at T=1330K are presented. The RPA curve lies above the WCA results and the GA term introduces further small increase. The ERPA term is too small to be observed as a separate curve in Fig.7b.

Figures 8a,b and 9a,b illustrate the behaviour of the low-k structure factor for Aluminium at lower temperatures: T=978K and near melting point at T=943K. In these two cases the reference system (WCA) describes the experimental S(k) rather well at small k. This has been noticed previously by Olsson and Dahlborg (1982, thereafter referred to as O&D). According to their suggestion it may be due to the high density of Al (Table I, column 9).

The results for the last case studied, Lead near melting point (T=613K) are presented in Fig.10a and b. Here the WCA results are closer to experiment than the RPA. The ERPA and, especially, the GA 'improve' this situation fractionally,

(Fig.10b) and these contributions are relatively higher than in the previous cases. Such behaviour may be related to the fact that Lead exhibits a more hard-sphere like repulsive part of the pairwise potential than the other metals studied. Also it should be pointed out that in our study the many-body and density dependent forces have been neglected, but in the case of Lead these may play an important role (McLaughlin and Young,1982a).

Experimental points drawn in Figs.6a, 9a and 10a are taken from Waseda (1980) and in Fig.8a from O&D. The experimental error in this k-region is about 10% (O&D, p.229). The contribution of the ERPA and GA to RPA, on the other hand, varies from ≈0.6% (Rb,T=1900K; Pb,T=613K) to ≈0.08% for Al,T=1330K. Clearly, with the present experimental abilities to perform measurements of the structure factor in the low-k region we must interpret the ERPA and the GA corrections as negligible.

Finally we present the contributions of the various terms to the inverse total structure factor in GA (Fig.11a, b, c) and ERPA (Fig.12a, b, c). The Figure of this type can be found in O&D, p.237 for Al,T=978K. There are few important differences in these two graphs (our Fig.11a and O&D Fig.5).

O&D reference system contribution is smaller than total 1/S(k) and RPA contributes positively, also their $1/S_{2Gask}$ term (dotted line) is of higher order of magnitude than ours. Fig.11a shows that in our case RPA contributes with negative sign and $1/S_{2Gask}$ term is only fractional part of the total 1/S. In fact it appears to be zero in Fig.11a, and only magnification in Fig.11c proves that $1/S_{2Gask}$ has very small, finite value.

Figures 13 and 14 represent similar decomposition of 1/S for GA and ERPA in a case of Aluminium at T=943K.

6.2 DISCUSSION AND CONCLUSIONS

The structure factor for three simple metals at various temperatures in the low-k region was calculated using the Gaskell's approximation. Comparisons were made with RPA and ERPA results. The effective pair potential derived from standard pseudopotential theory was used. The pseudopotential was modeled by a simple, local Ashcroft empty-core form and the screening of electrons was accounted within Vashishta and Singwi form of dielectric function. The pair potential exhibited typical oscillatory behaviour in its long range part. This well-known and tested pair potential was used to study the validity of the Gaskell's approximation. The contribution of the terms representing the coupling of the density fluctuations of different wavevectors was found to be less than 1% of the RPA values in all cases studied.

The different result of D&O for Al,T=978K (1982-Fig.5) can be explained if one notices that they used r^{-12} reference system (as opposed to our WCA-soft sphere) and the perturbing tail of the potential was modelled by a function dependent on six adjustable parameters which varied from a one-period oscillatory to a simple exponential one.

It is a known fact that there is some arbitrarness in the potential $\psi_1(r)$ for separations ,r, less than the position of the principal minimum r_0, and so calculations were performed, were the value of $\psi_1(r)$ for $r<r_0$ was zero instead of $\psi_1(r_0)$ – this corresponds to type I potential as defined by O&D (1982–see their Fig.2). Although the absolute values of RPA, ERPA and GA contributions to the total structure factor were changed, the relative magnitude of ERPA and GA corrections were again negligible (less than 1%). Because of the purly manipulational character of this trial we do not include the detailed results.

It can be mentioned at this point that the study of different systems – liquid argon and neon – by means of ERPA, where the pair potential was modelled by double Yukawa form (Datta,1983) also led the author to the similar conclusion that:"Compressibility values in the RPA and ERPA are almost identical, indicating that the ERPA does not represent any significant improvement over the RPA, at least for this particular long wave property"(Datta,1983,p.1021).

The formal reason for the smallness of the correlational contribution in ERPA and GA is that the integral in Eqs.(4.1.17) and (4.2.16) in both cases includes the expression:

$$\psi_1(q)(S_0(|\underline{q}-\underline{k}|) - 1)$$

Fig.2 shows that $\psi_1(q)$ factor exhibits tiny oscillations about zero. The structure factor $S_0(k)$ is a function oscillating about unity, so the term $(S_0(|\underline{q}-\underline{k}|) - 1)$ quickly reaches values close to zero, and the integral in both ERPA and GA expressions is quickly convergent and of very small value.

It is a known fact that the WCA reference system is not well suited for alkalis at temperatures near melting point. Liquid alkali metals have too soft core part of the potential. Nevertheless at high temperatures the hard-sphere type of description (e.g.WCA) is expected to be satisfactory,(McLaughlin and Young,1984a). It is argued on general theoretical grounds that:"..a typical binary collision involves the conversion of $\sim k_B T$ of kinetic energy into potential energy and so a steeper part of the interatomic potential curve is probed as T increases. Thus the core and therefore the large-k part of the structure factor take on more of a hard-sphere character",(McLaughlin and Young,1984a, p.2).

For lower temperatures alkalis can be described satisfactory by other reference systems like the OCP or the CHS. It is a matter of the new computational tests to say wheather the low-k structure factor in the GA is sensitive on the reference system chosen,(the integral term involves S_0^2).

Both ERPA and GA are only zeroth order theories (see Eqs.(4.1.7) and (4.2.4)). It was demonstrated in another context (Chakravarty and Woo,1976) that using iteration methods and integrating the Gaskell type of expression (Eq.4.2.4) did not essentialy improve the zeroth order approximation. It is difficult to say whether similar procedure (full integration of Eq.4.2.4 with respect to coupling parameter μ) would bring a new result. Similarily it is impossible, without carrying numerical tests, to judge the importance of the next term of the McLaurin expansion that was derived in Appendix A.

The results presented in this thesis for Gaskell's Approximation has not been obtained earlier for simple liquid metals that are characterized by the effective pair-potential derived from pseudopotential theory. To the author's best knowledge the only attempt to use GA in liquid metal theory was made by Olsson and Dahlborg (1982). However, as pointed out earlier, they were essentially attempting to find a crude effective potential by fitting experimental results. We are confident that our results are based on systematic, physical assumptions about the effective pair potential developed between the ions. The Friedel oscillations were included in all computations and aimed at explaining the role and importance of the long range part of the pair-potential on the low-k region of the static structure factor. The ERPA and GA were tested and also compared with the MDA results obtained by McLaughlin and Young (1982a, 1984a,b). From the evidence given it appears that MDA is superior to ERPA and GA. In all cases studied both ERPA and GA corrections to RPA results are negligible.

Appendix A

THE SECOND ORDER PARTIAL DERIVATIVE OF THE STRUCTURE FACTOR WITH RESPECT TO THE COUPLING PARAMETER μ

We present here the final expression for the second order partial derivative of the structure factor appearing in Eq.(4.2.21). This can be written:

$$\frac{\partial^2}{\partial\mu^2}S_\mu(q)=(\beta^2/4)\sum_{\underline{k}}\sum_{\underline{w}}\psi_1(k)\psi_1(w)[\langle N^{-3}|\rho_{\underline{k}}|^2|\rho_{\underline{q}}|^2|\rho_{\underline{w}}|^2\rangle_\mu$$

$$-\ S_\mu(q)\langle N^{-2}|\rho_{\underline{k}}|^2|\rho_{\underline{w}}|^2\rangle_\mu - S_\mu(k)\langle N^{-2}|\rho_{\underline{q}}|^2|\rho_{\underline{w}}|^2\rangle_\mu$$

$$-\ S_\mu(w)\langle N^{-2}|\rho_{\underline{k}}|^2|\rho_{\underline{q}}|^2\rangle_\mu + 2S_\mu(k)S_\mu(q)S_\mu(w)] \qquad (A.1)$$

The double sum can be further split into five groups:

1) $\underline{q}=\pm\underline{k}=\pm\underline{w}$;

2) $\underline{q}=\pm\underline{k}$ and $\underline{q},\underline{k}\neq\pm\underline{w}$

3) $\underline{q}=\pm\underline{w}$ and $\underline{q},\underline{w}\neq\pm\underline{k}$

4) $\underline{w}\neq\pm\underline{q}\neq\pm\underline{k}$ and $\underline{w}=\pm\underline{k}$

5) $\underline{w}\neq\pm\underline{q}\neq\pm\underline{k}\neq\pm\underline{w}$

It is easy to see that groups 2) and 3) are equivalent. Now the procedure described by Eqs.(4.2.12')-(4.2.15) may be again applied to formula (A.1) and this yields quite a lengthy expression which involves the terms of the type:

$$\langle N^{-3}|\rho_{\underline{q}}|^6\rangle_\mu\ ,\qquad \langle N^{-3}|\rho_{\underline{q}}|^4|\rho_{\underline{k}}|^2\rangle_\mu$$

and $\langle N^{-3}|\rho_{\underline{q}}|^2|\rho_{\underline{k}}|^2|\rho_{\underline{w}}|^2\rangle_\mu$

These terms represent the sixth order density correlation functions. The structure of (A.1) is identical to that of the hierarchy of expansions (1) in Wu (1971a) and to Ursell-Mayer expansion.

Appendix B

THE PRACTICAL METHOD OF CALCULATING $\psi_1(q)$

As we mentioned in Chapter 5 relatively small Friedel oscillations exhibited by a tail of the effective pair potential should be treated with special care when $\psi_1(r)$ is transformed back to q-space. The method which avoids straight Fourier transformation of $\psi_1(r)$ was presented by McLaughlin and Young (1982a). We applied this calculational method in our study and we quote it here for sake of completness.

With the separation of the potential given by Eqs.(3.2.1)-(3.2.2) we write a Fourier transform of the tail of the potential in the following way:

$$\begin{aligned}\psi_1(q)-\psi(q)&=\int_0^{r_0} dr\,4\pi r^2\,\frac{\sin qr}{qr}\{\psi(r_0)-\psi(r)\}\\ &=\frac{4\pi}{q^3}(\sin qr_0-qr_0\cos qr_0)\psi(r_0)\\ &-(\pi q)^{-1}\int_0^{\infty} dk\,k\,\psi(k)\left(\frac{\sin(q-k)r}{q-k}-\frac{\sin(q+k)r}{q+k}\right)\end{aligned}\qquad (B.1)$$

One substitutes the expression (5.18) in (B.1) and after some integrations and simple manipulations one arrives at the result:

$$\begin{aligned}\psi_1(q)=\frac{4\pi}{q^3}&(\sin qr_0-qr_0\cos qr_0)\psi(r_0)\\ &-\frac{4\pi Z^2}{q^2}(F_N(q)-\cos qr_0)\\ &+\frac{4Z^2}{q}\int_0^{\infty} dk\,\frac{F_N(k)}{k}\left\{\frac{\sin(q-k)r_0}{q-k}-\frac{\sin(q+k)r_0}{q+k}\right\}\end{aligned}\qquad (B.2)$$

For q=0 one finds the limit $\psi_1(q=0)$:

$$\psi_1(q=0) = 4/3\ \pi r_0^{\,3}\ (\psi(r_0) + \frac{6Z^2}{\pi}\int_0^\infty dk F_N(k) \frac{(\sin kr_o - kr_o \cos kr_o)}{(kr_0)})$$

$$- 2\pi Z^2 r_0^{\,2} + \psi(q=0) \qquad (B.3)$$

where

$$\psi(q=0) = 4\pi Z^2 (r_c^{\,2} + \frac{\pi}{4k_F} - \frac{AB}{k_F^2}) \qquad (B.4)$$

(see McLaughlin and Young,1982a).

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TABLE I

INPUT DATA

1	2	3	4	5	6	7	8	9
METAL	VALENCY Z	TEMPERATURE T [K]	FERMI RADIUS k_F $[a_0]$	r_S $[a_0]$	V-S PARAMETER A	V-S PARAMETER B	ASHCROFT EMPTY CORE DIAMETER R_c $[a_0]$	NUMBER DENSITY $\rho \times 10^{-3} [a_0^{-3}]$
RUBIDIUM a)	1	1900.0	0.2705	7.0962	1.35	0.238	2.45	0.6681
RUBIDIUM b)	1	1900.0	0.2705	7.0962	1.35	0.238	2.60	0.6681
RUBIDIUM	1	350.0	0.3565	5.3826	1.2127	0.2635	2.48	1.5309
RUBIDIUM	1	313.0	0.3568	5.3779	1.2123	0.2636	2.45	1.5349
ALUMINIUM	3	1330.0	0.8723	2.2000	0.8796	0.3258	1.12	7.4734
ALUMINIUM	3	978.0	0.8852	2.1680	0.8757	0.3266	1.12	7.8088
ALUMINIUM	3	943.0	0.8867	2.1642	0.8752	0.3267	1.12	7.8500
LEAD	4	613.0	0.8161	2.3515	0.8982	0.3217	1.47	4.5900

TABLE II

1	2	3	4	5
METAL	TEMPERATURE T [K]	OCCURENCE OF THE MINIMUM OF THE POTENTIAL R_{Min} [a_0]	VALUE OF THE POTENTIAL AT THE FIRST MINIMUM $V(R_{Min})$ [a.u. x 10^{-2}]	HARD CORE DIAMETER σ [a_0]
RUBIDIUM a)	1900.0	9.10	-0.4106	7.2769
RUBIDIUM b)	1900.0	9.60	-0.3531	7.6296
RUBIDIUM	350.0	9.41	-0.2182	8.3388
RUBIDIUM	313.0	9.31	-0.2213	8.3085
ALUMINIUM	1330.0	5.43	-0.1525	4.8899
ALUMINIUM	978.0	5.42	-0.1200	4.9345
ALUMINIUM	943.0	5.42	-0.1161	4.9396
LEAD	613.0	5.99	-0.7795	5.7462

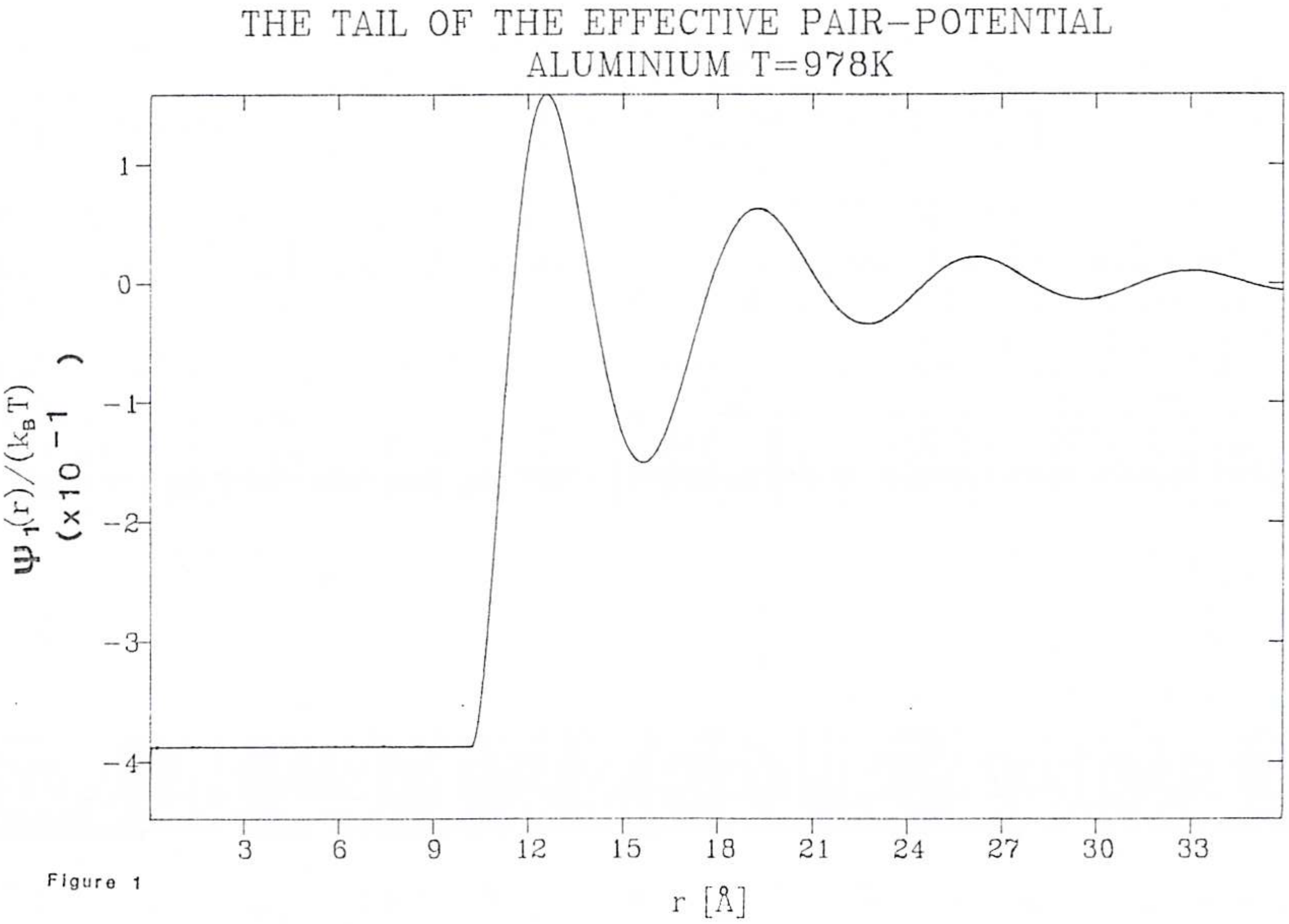

THE TAIL OF THE EFFECTIVE PAIR-POTENTIAL
ALUMINIUM T=978K
$\psi_1(r)/(k_B T)$
$(\times 10^{-1})$
1
0
-1
-2
-3
-4
3
6
9
12
15
18
21
24
27
30
33
r [Å]

Figure 1

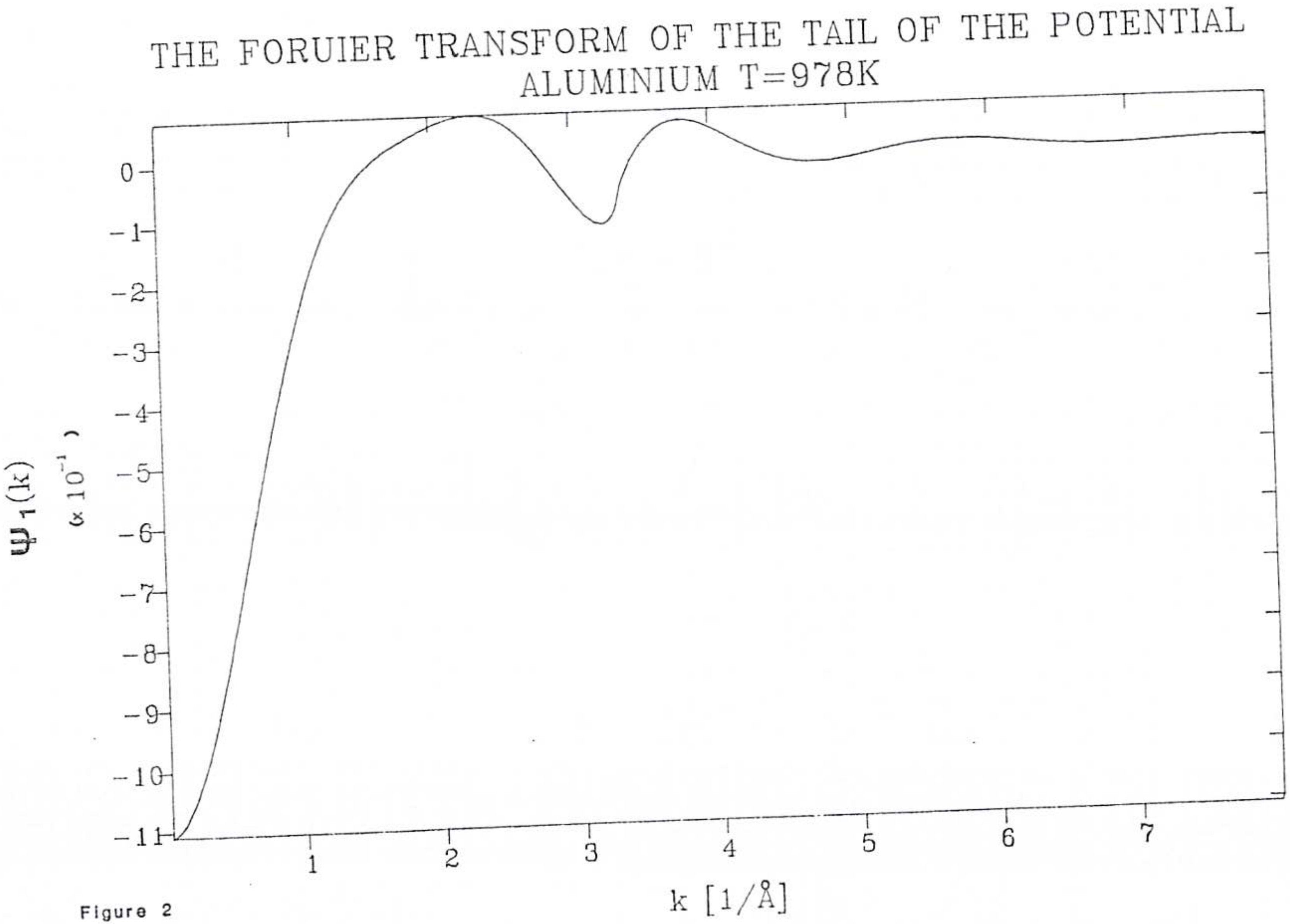

THE FORUIER TRANSFORM OF THE TAIL OF THE POTENTIAL
ALUMINIUM T=978K
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
$\Psi_1(k)$
(x 10^{-1})
1
2
3
4
5
6
7
k [1/Å]

Figure 2

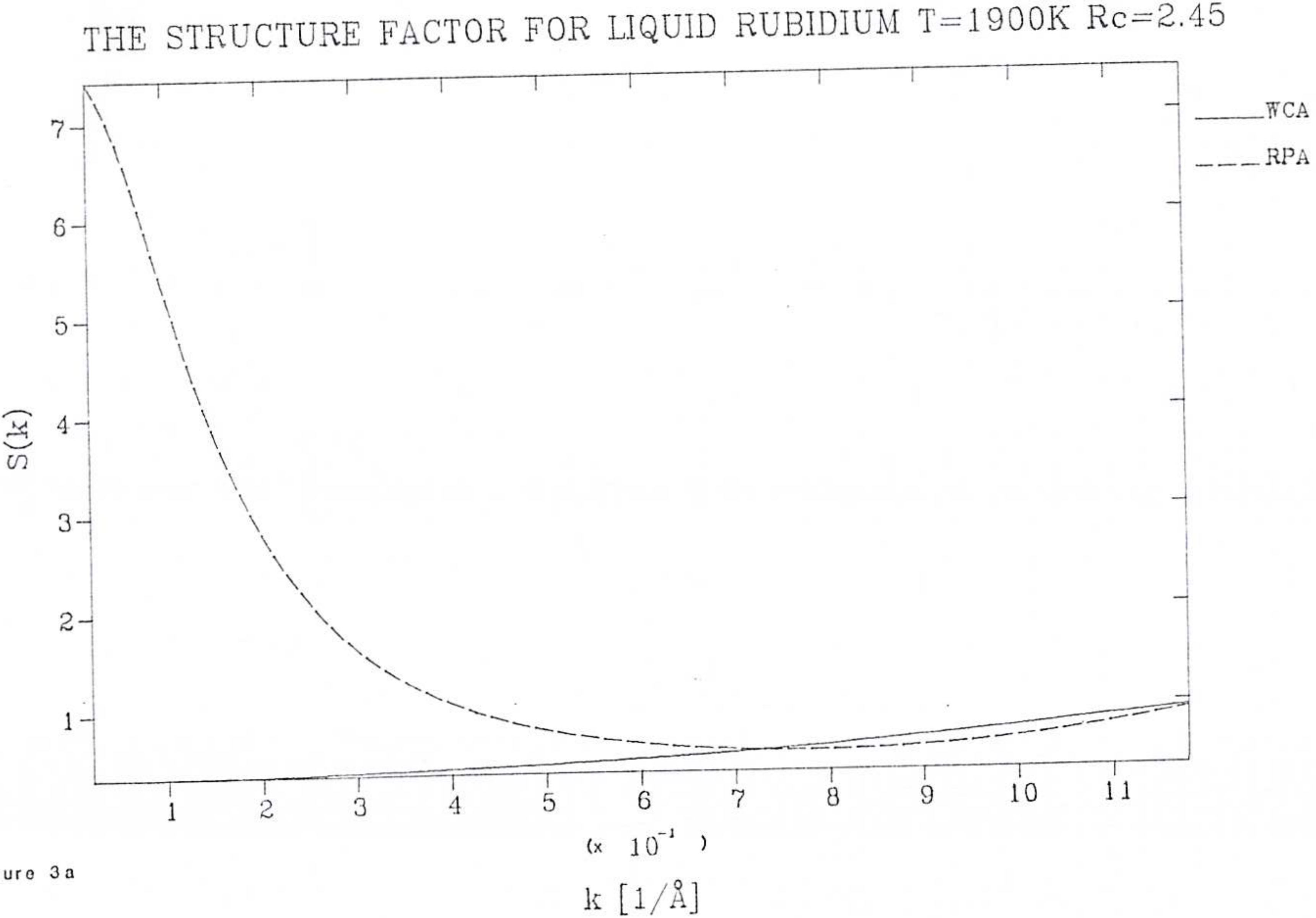

THE STRUCTURE FACTOR FOR LIQUID RUBIDIUM T=1900K Rc=2.45
S(k)
7
6
5
4
3
2
1
1
2
3
4
5
6
7
8
9
10
11
(x 10^{-1})
k [1/Å]
WCA
RPA

Figure 3a

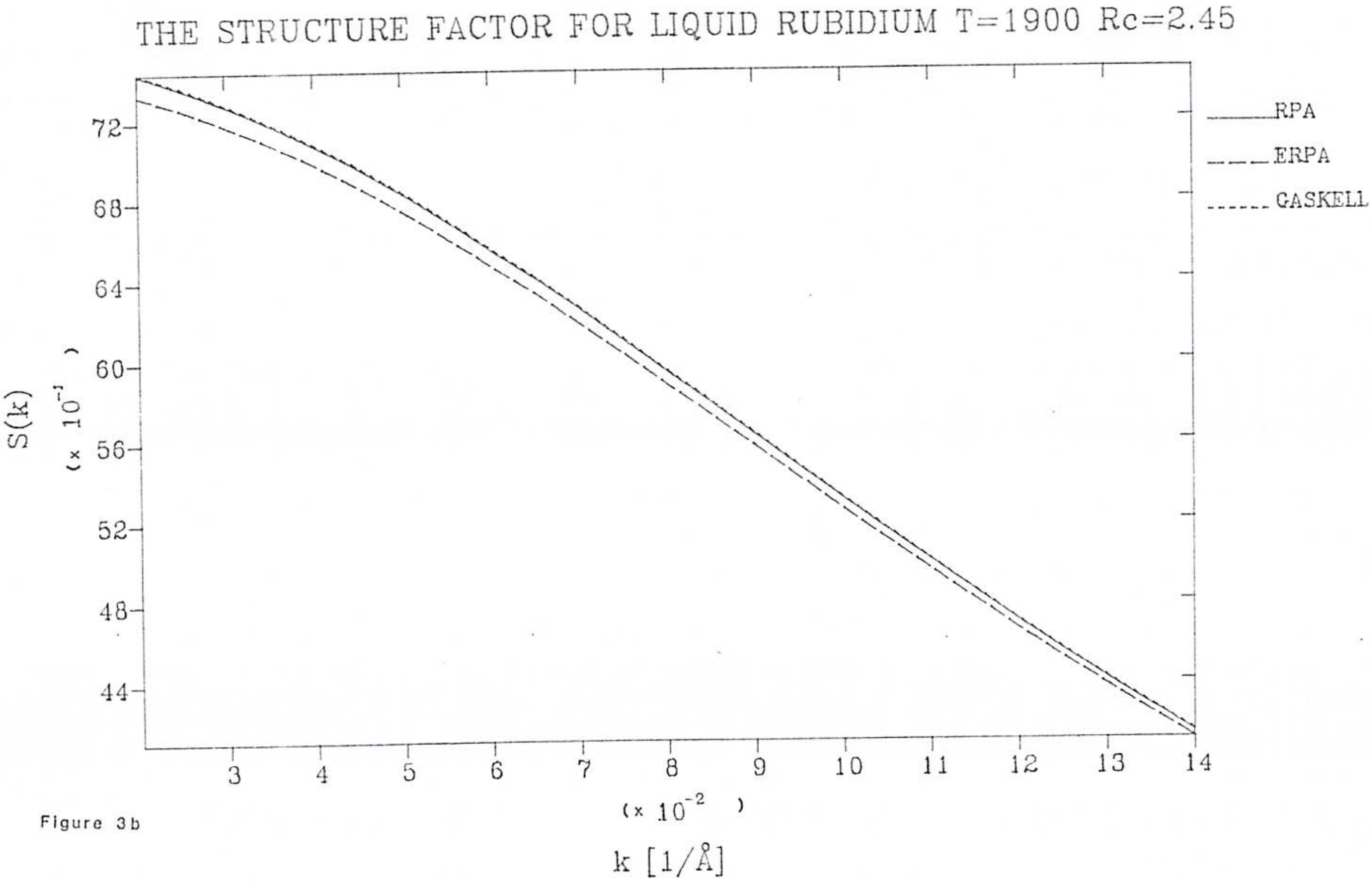

THE STRUCTURE FACTOR FOR LIQUID RUBIDIUM T=1900 Rc=2.45
S(k)
(× 10^-1)
72
68
64
60
56
52
48
44
3
4
5
6
7
8
9
10
11
12
13
14
(× 10^-2)
k [1/Å]
RPA
ERPA
GASKELL

Figure 3b

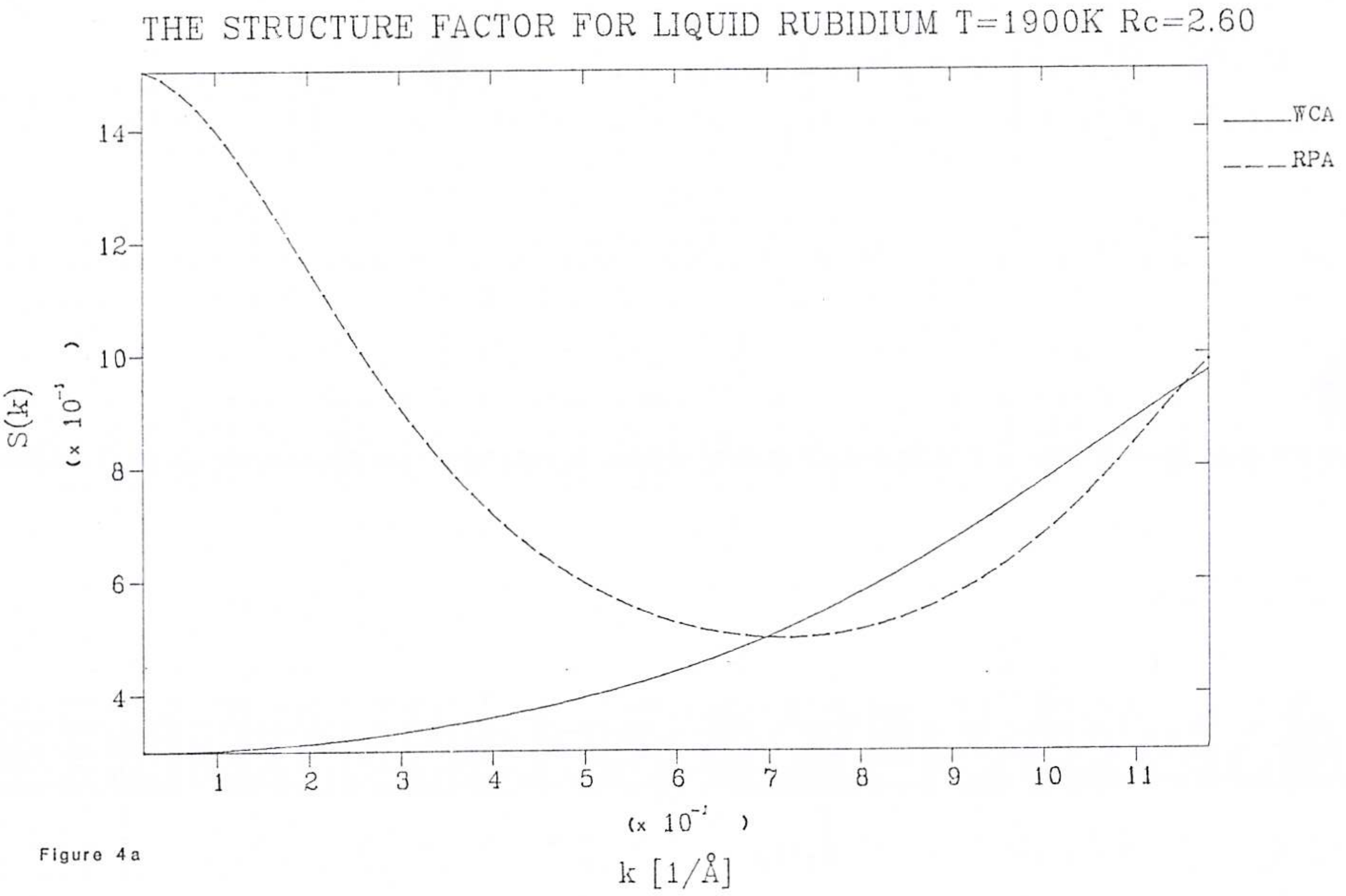

THE STRUCTURE FACTOR FOR LIQUID RUBIDIUM T=1900K Rc=2.60
S(k)
(x 10^-1)
14
12
10
8
6
4
1
2
3
4
5
6
7
8
9
10
11
(x 10^-1)
k [1/Å]
WCA
RPA

Figure 4a

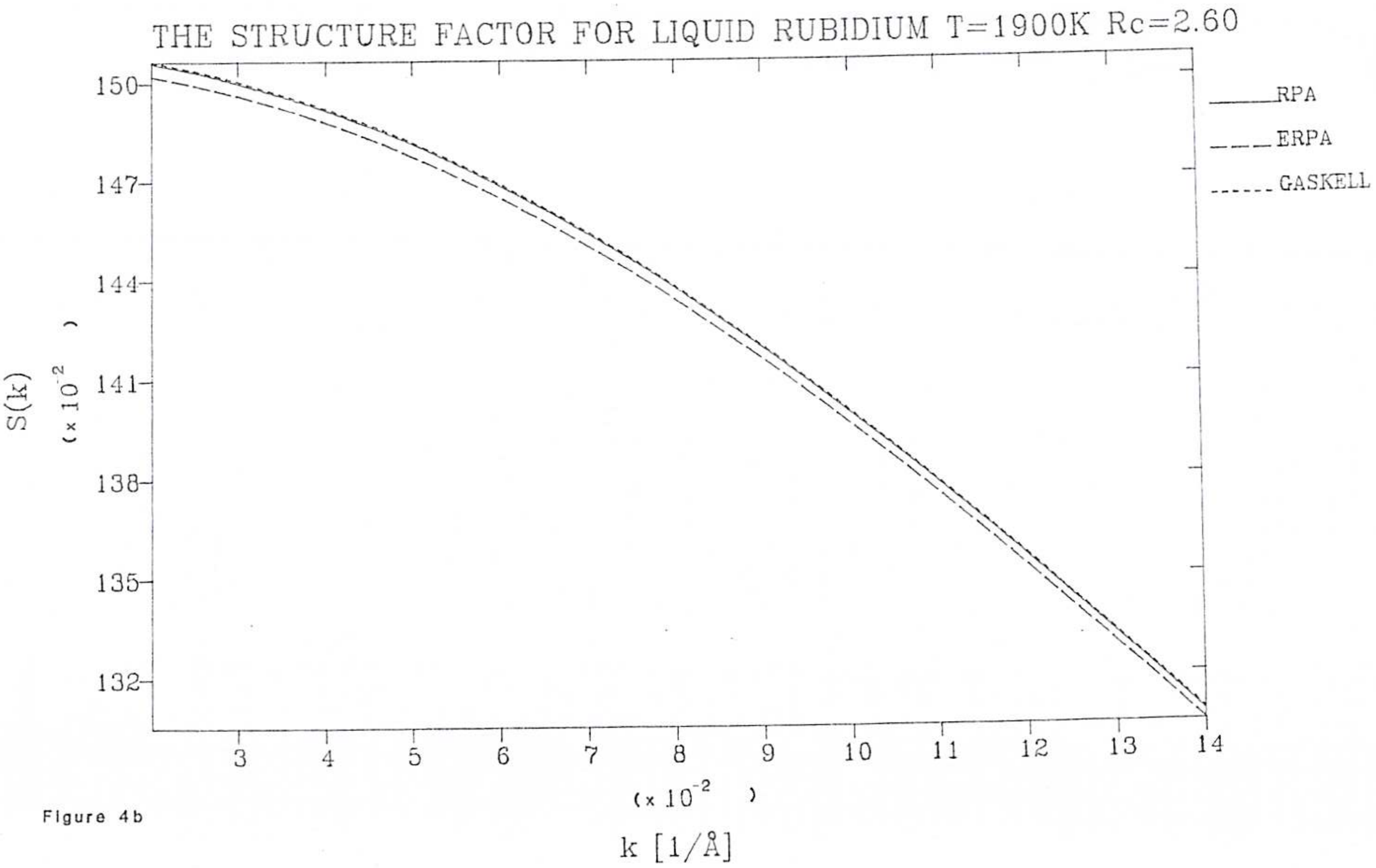

THE STRUCTURE FACTOR FOR LIQUID RUBIDIUM T=1900K Rc=2.60
RPA
ERPA
GASKELL
S(k)
(× 10^{-2})
150
147
144
141
138
135
132
3
4
5
6
7
8
9
10
11
12
13
14
(× 10^{-2})
k [1/Å]

Figure 4b

THE STRUCTURE FACTOR FOR LIQUID RUBIDIUM T=350K Rc=2.48

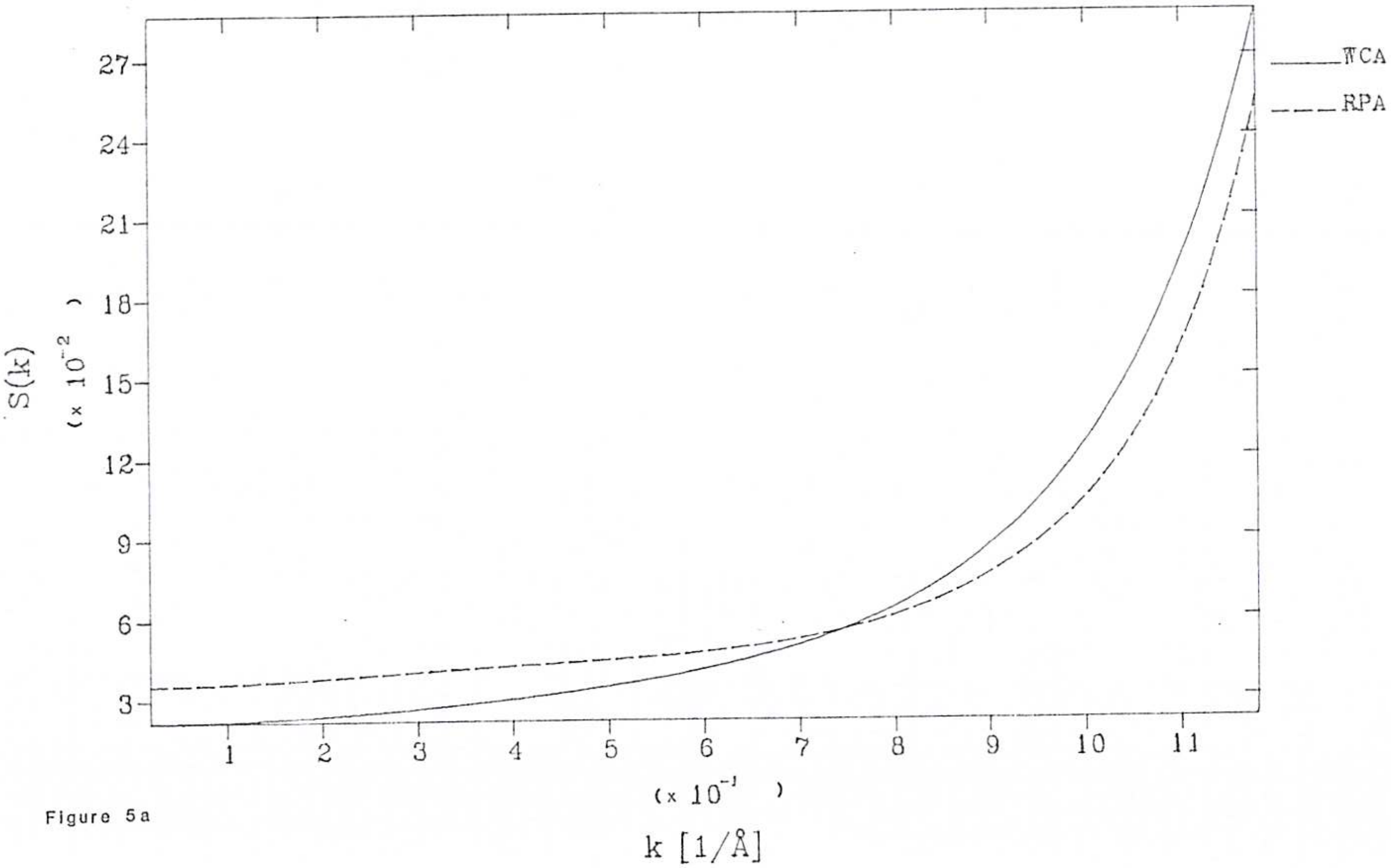


Figure 5a

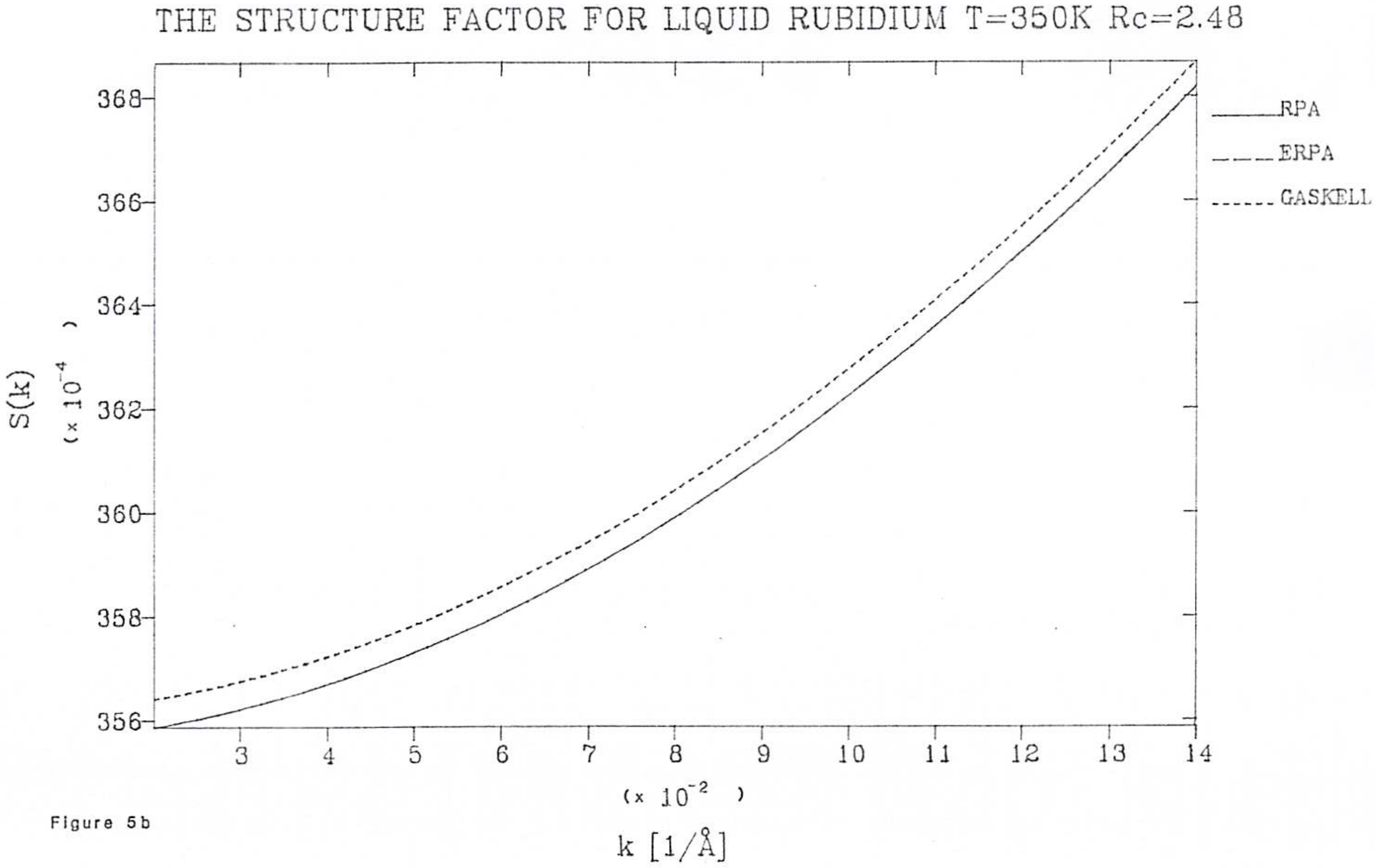

THE STRUCTURE FACTOR FOR LIQUID RUBIDIUM T=350K Rc=2.48
368
366
364
362
360
358
356
S(k)
(× 10⁻⁴)
3
4
5
6
7
8
9
10
11
12
13
14
(× 10⁻²)
k [1/Å]
RPA
ERPA
GASKELL

Figure 5b

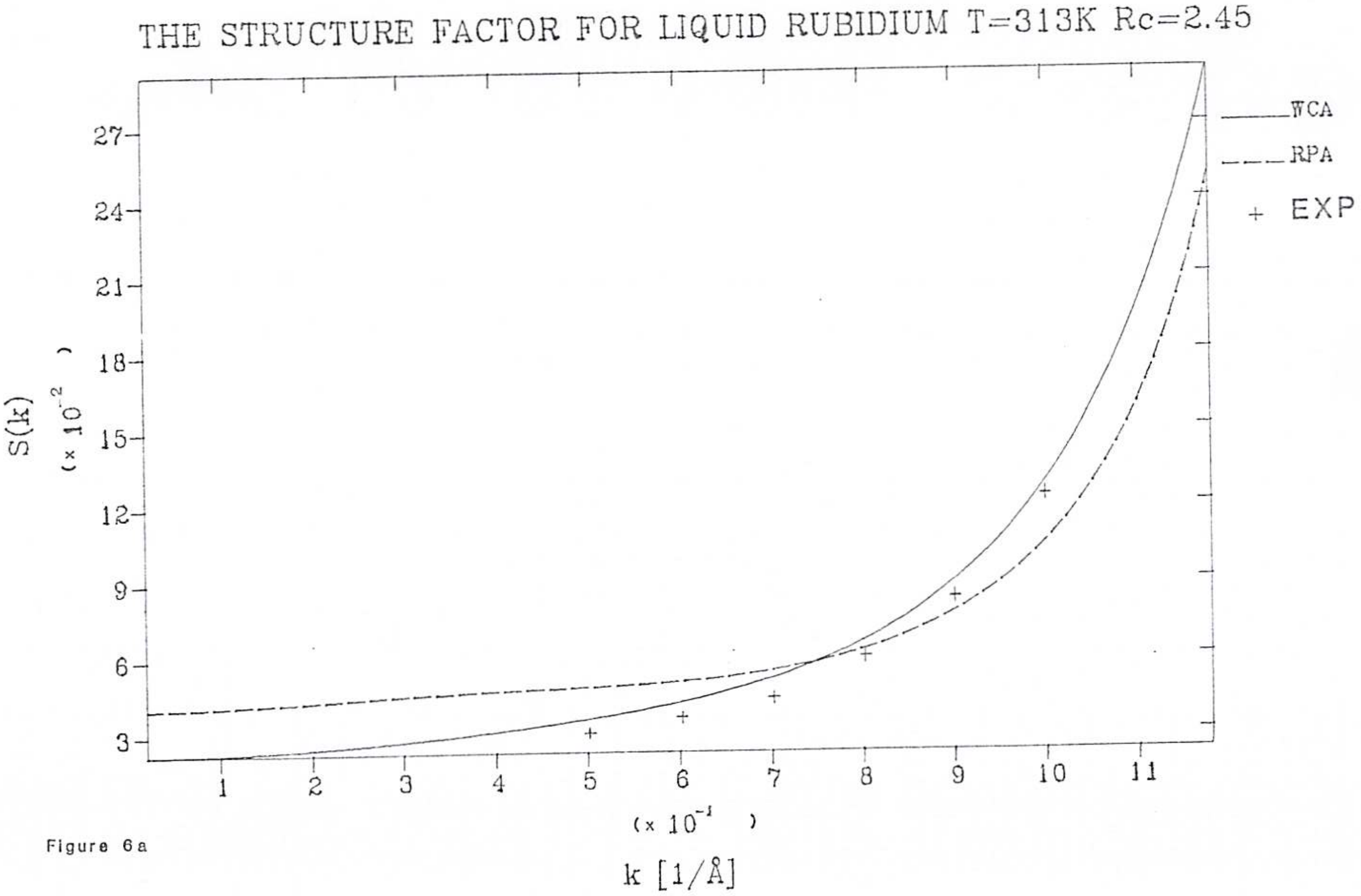

THE STRUCTURE FACTOR FOR LIQUID RUBIDIUM T=313K Rc=2.45
WCA
RPA
+ EXP
S(k)
(× 10^-2)
27
24
21
18
15
12
9
6
3
1
2
3
4
5
6
7
8
9
10
11
(× 10^-1)
k [1/Å]

Figure 6a

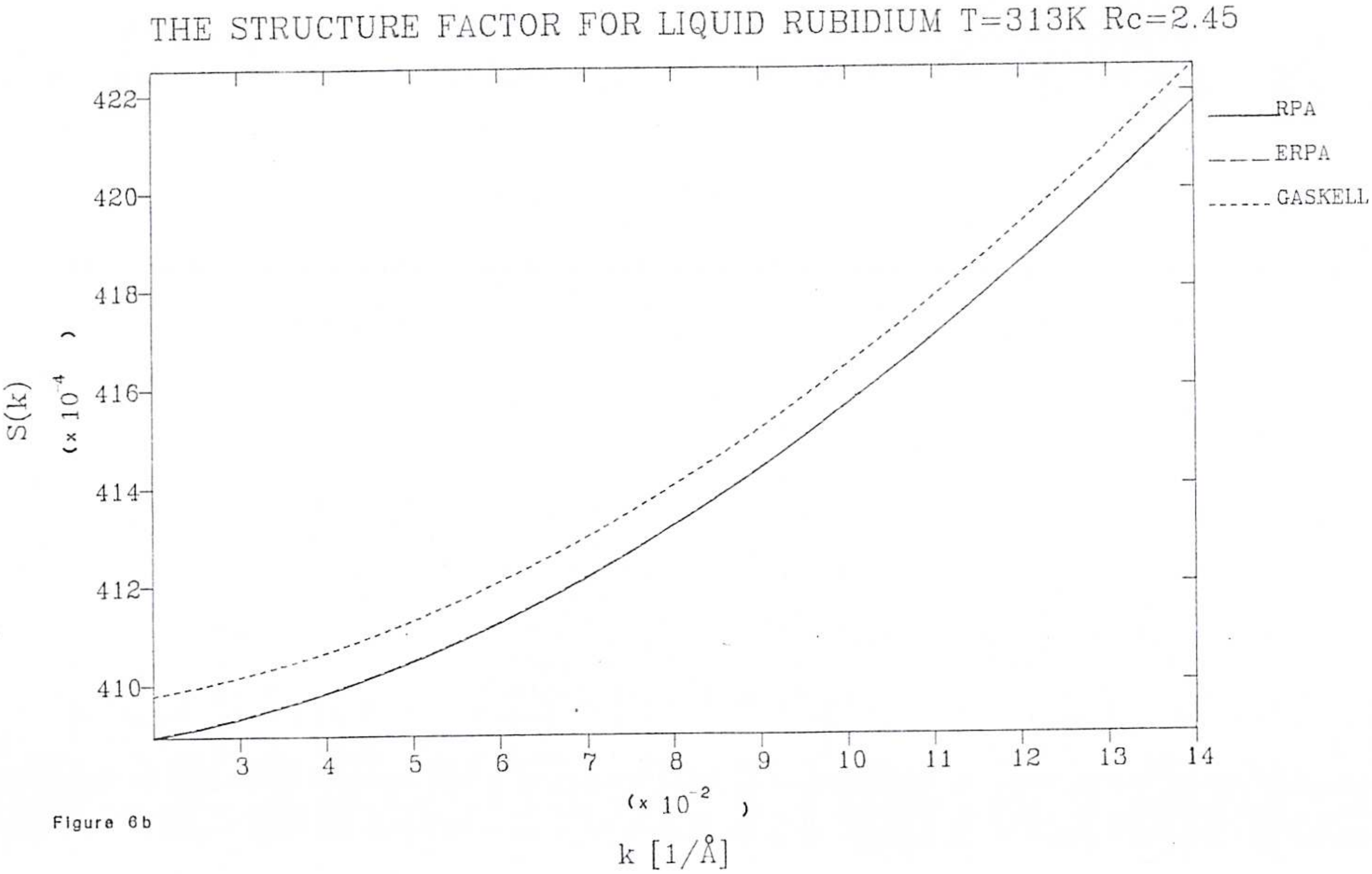

THE STRUCTURE FACTOR FOR LIQUID RUBIDIUM T=313K Rc=2.45
422
420
418
416
414
412
410
S(k)
(× 10^-4)
3
4
5
6
7
8
9
10
11
12
13
14
(× 10^-2)
k [1/Å]
RPA
ERPA
GASKELL

Figure 6b

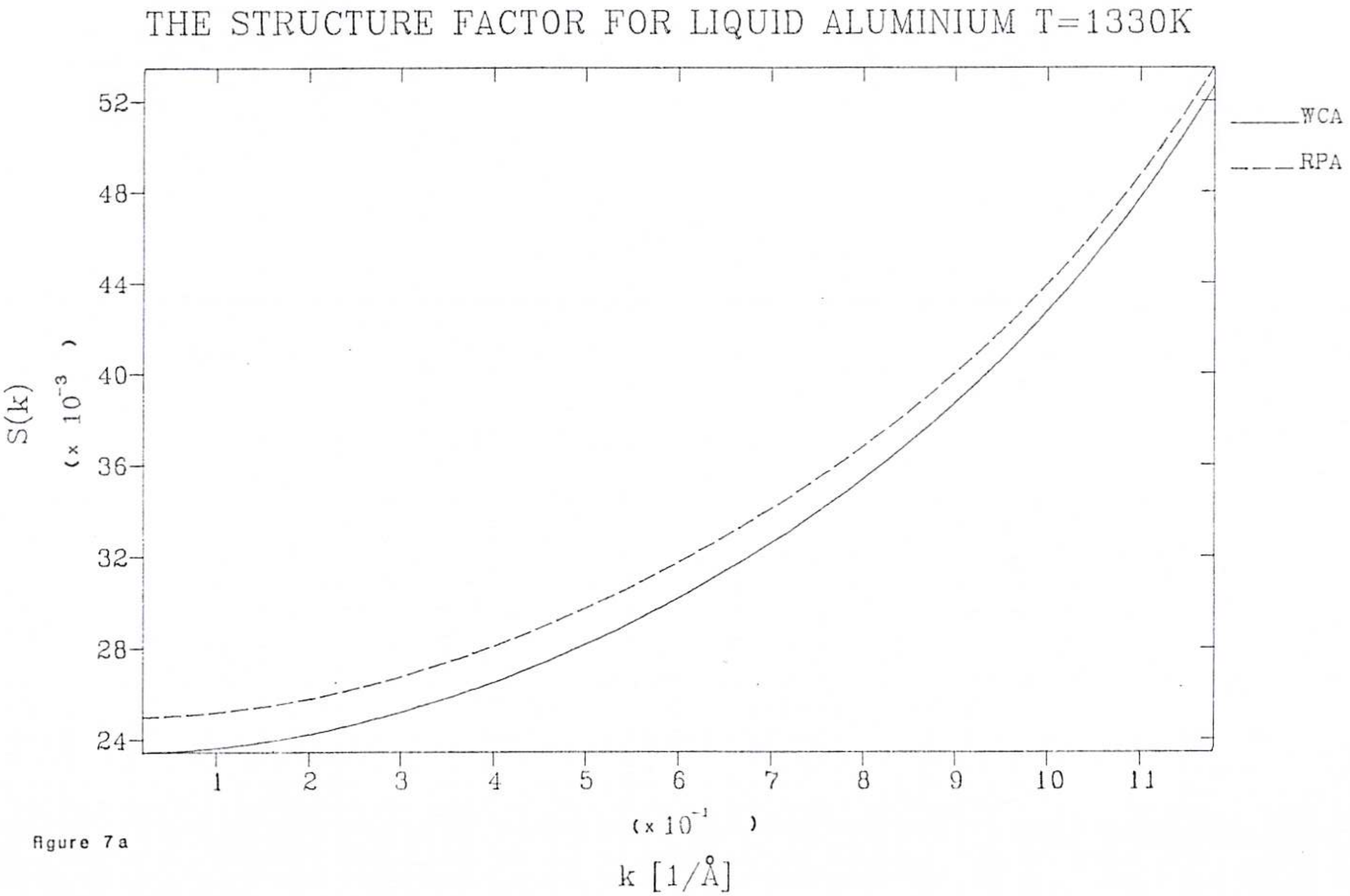

THE STRUCTURE FACTOR FOR LIQUID ALUMINIUM T=1330K
52
48
44
40
36
32
28
24
S(k)
(× 10^-3)
1
2
3
4
5
6
7
8
9
10
11
(× 10^-1)
k [1/Å]
WCA
RPA

Figure 7a

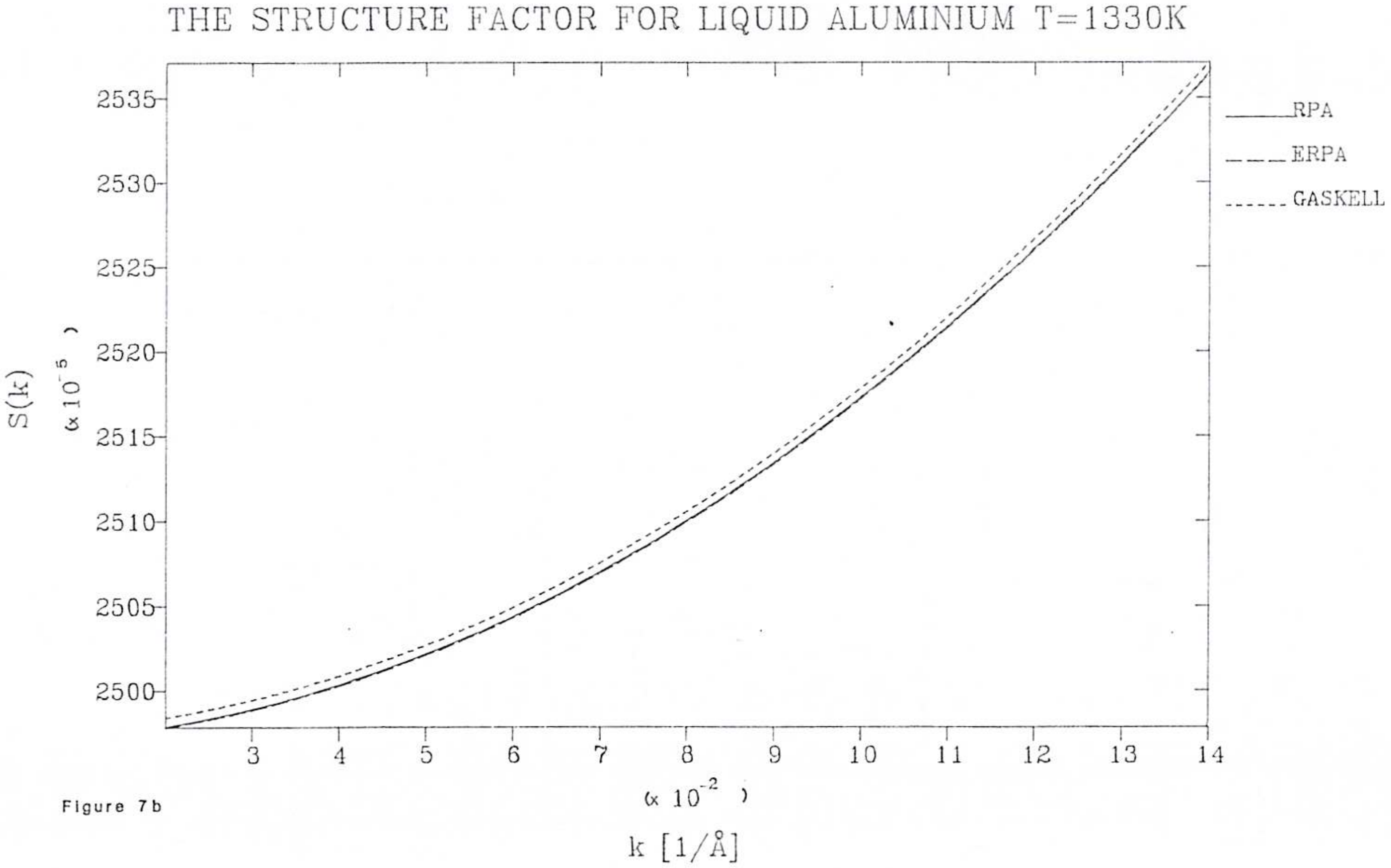

THE STRUCTURE FACTOR FOR LIQUID ALUMINIUM T=1330K
S(k)
(x 10^-5)
2535
2530
2525
2520
2515
2510
2505
2500
3
4
5
6
7
8
9
10
11
12
13
14
(x 10^-2)
k [1/Å]
RPA
ERPA
GASKELL

Figure 7b

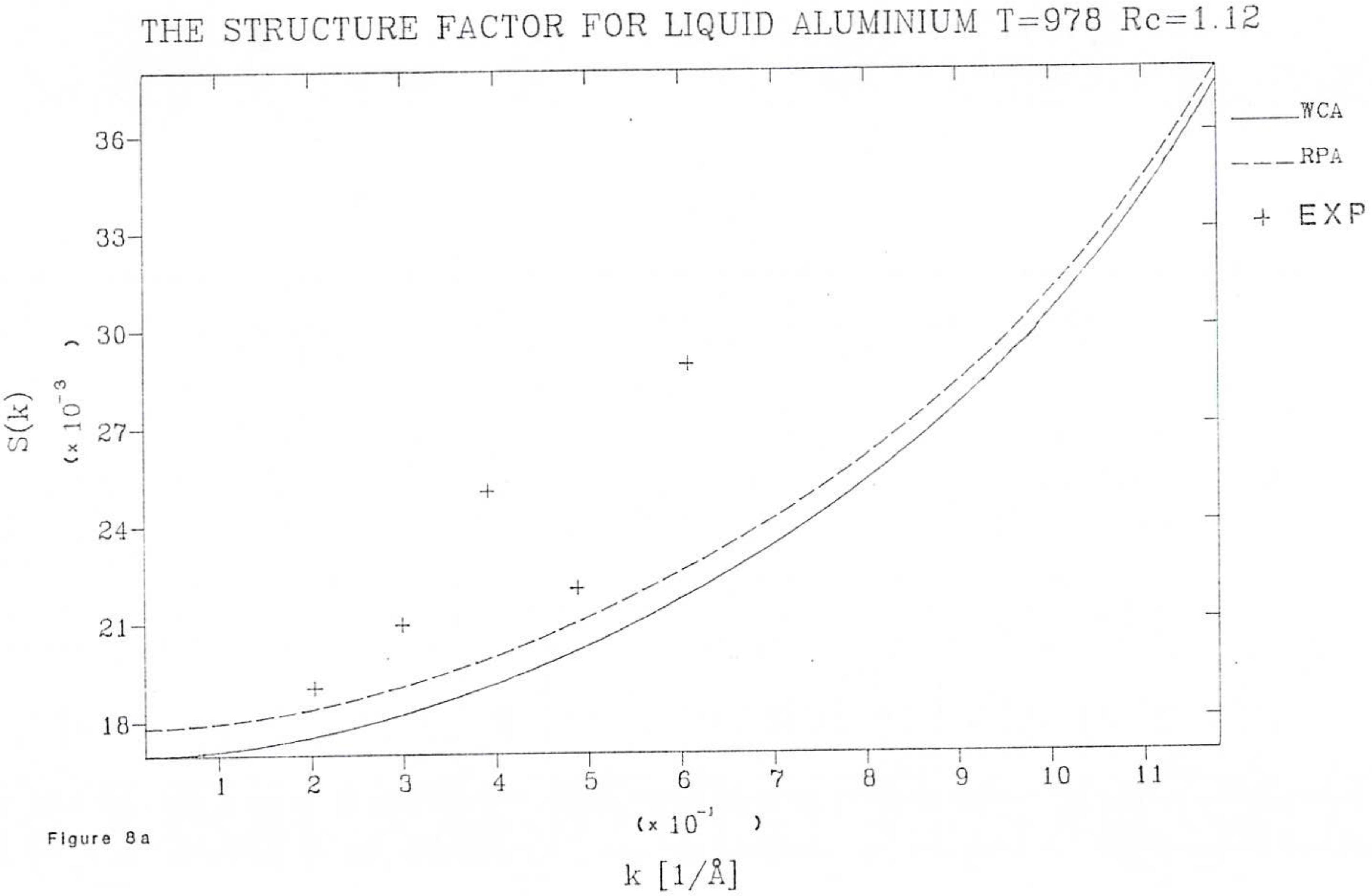

THE STRUCTURE FACTOR FOR LIQUID ALUMINIUM T=978 Rc=1.12
WCA
RPA
+ EXP
S(k)
(x 10^-3)
36
33
30
27
24
21
18
1
2
3
4
5
6
7
8
9
10
11
(x 10^-1)
k [1/Å]

Figure 8a

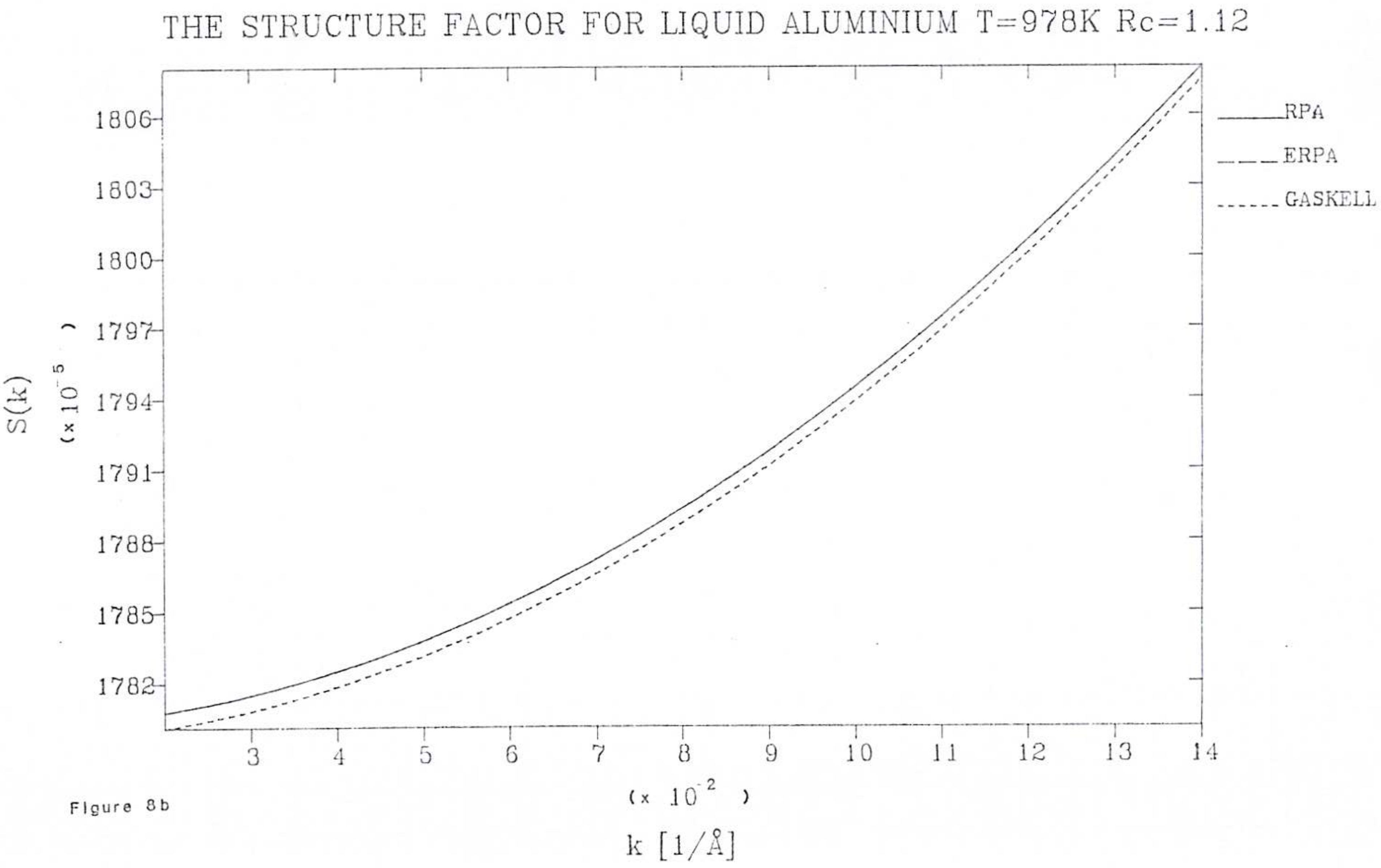

THE STRUCTURE FACTOR FOR LIQUID ALUMINIUM T=978K Rc=1.12
S(k)
(x 10⁻⁵)
1806
1803
1800
1797
1794
1791
1788
1785
1782
3
4
5
6
7
8
9
10
11
12
13
14
(x 10⁻²)
k [1/Å]
RPA
ERPA
GASKELL

Figure 8b

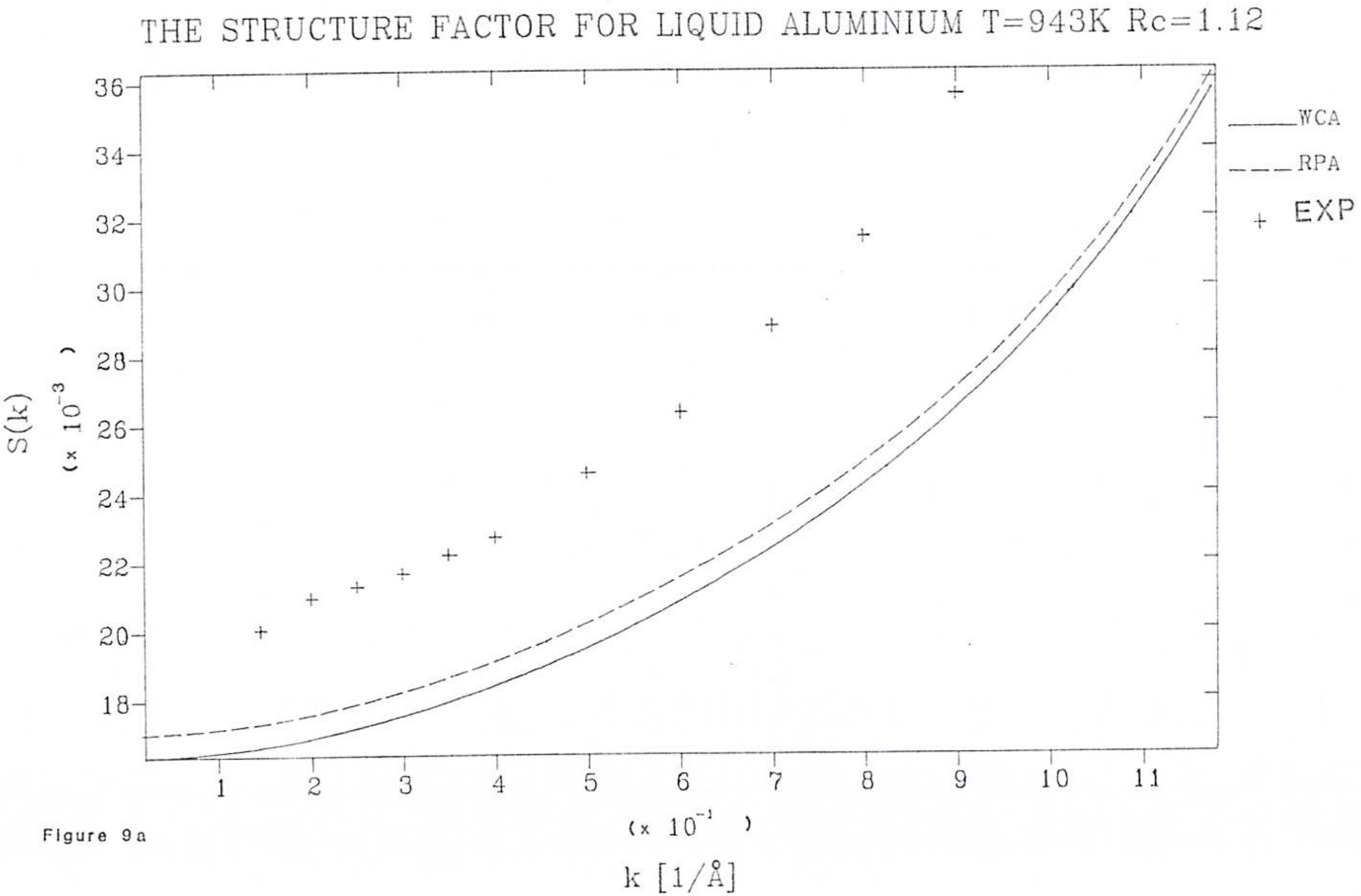

THE STRUCTURE FACTOR FOR LIQUID ALUMINIUM T=943K Rc=1.12
S(k)
(x 10^{-3})
36
34
32
30
28
26
24
22
20
18
1
2
3
4
5
6
7
8
9
10
11
(x 10^{-1})
k [1/Å]
WCA
RPA
+ EXP

Figure 9a

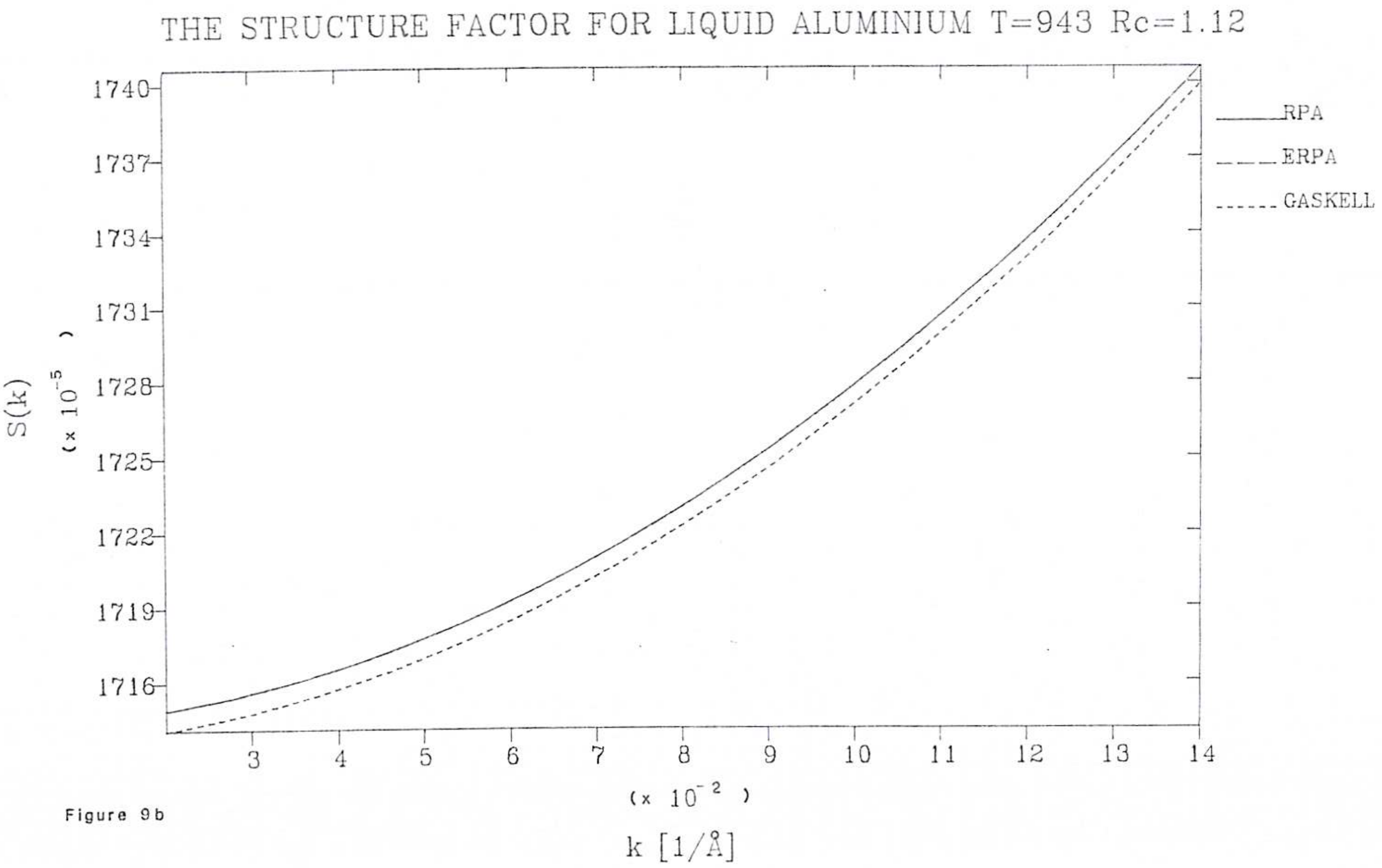

THE STRUCTURE FACTOR FOR LIQUID ALUMINIUM T=943 Rc=1.12
1740
1737
1734
1731
1728
1725
1722
1719
1716
S(k) (× 10⁻⁵)
3
4
5
6
7
8
9
10
11
12
13
14
(× 10⁻²)
k [1/Å]
RPA
ERPA
GASKELL

Figure 9b

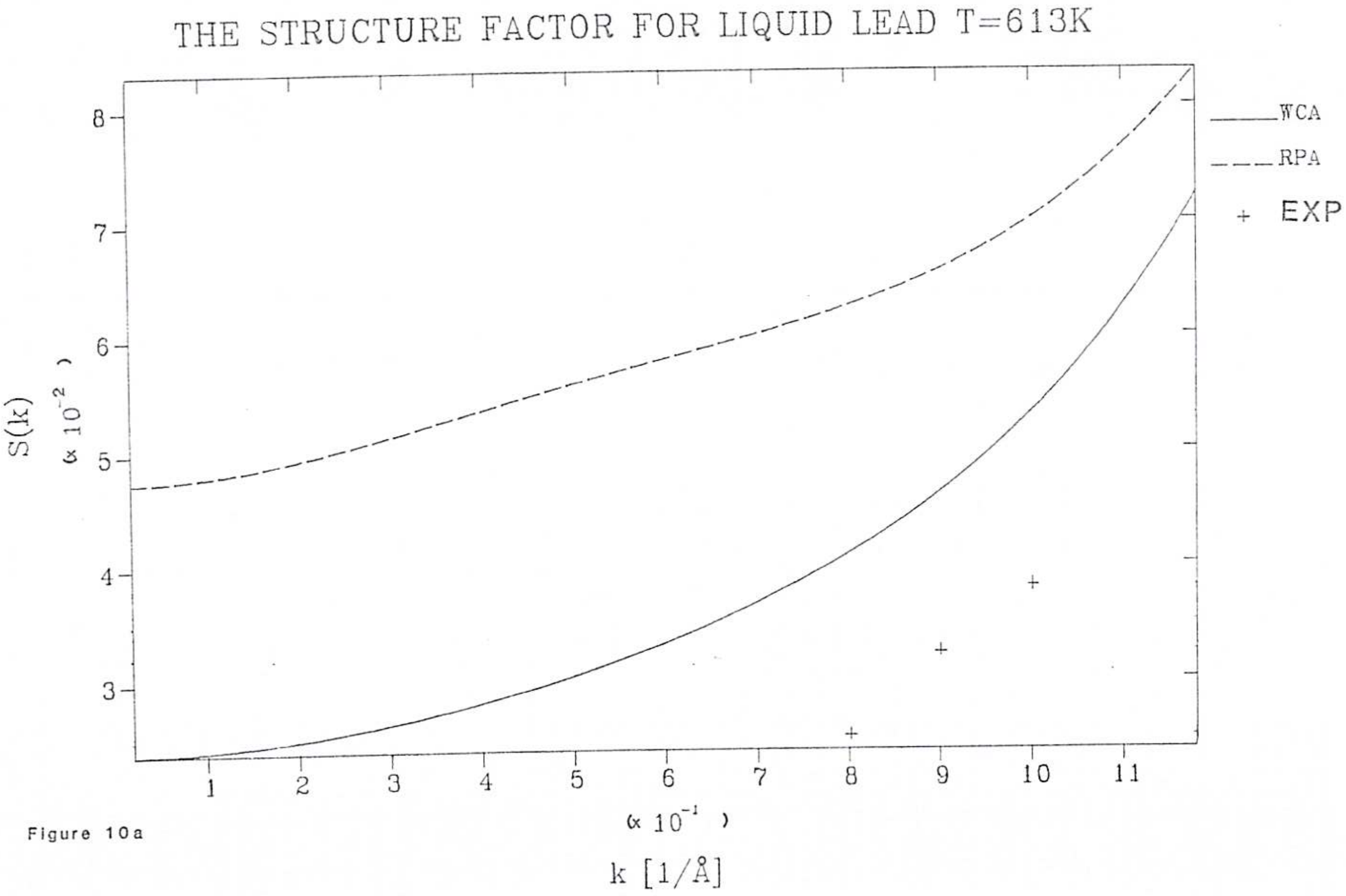

THE STRUCTURE FACTOR FOR LIQUID LEAD T=613K
WCA
RPA
+ EXP
S(k)
(x 10^-2)
8
7
6
5
4
3
1
2
3
4
5
6
7
8
9
10
11
(x 10^-1)
k [1/Å]

Figure 10a

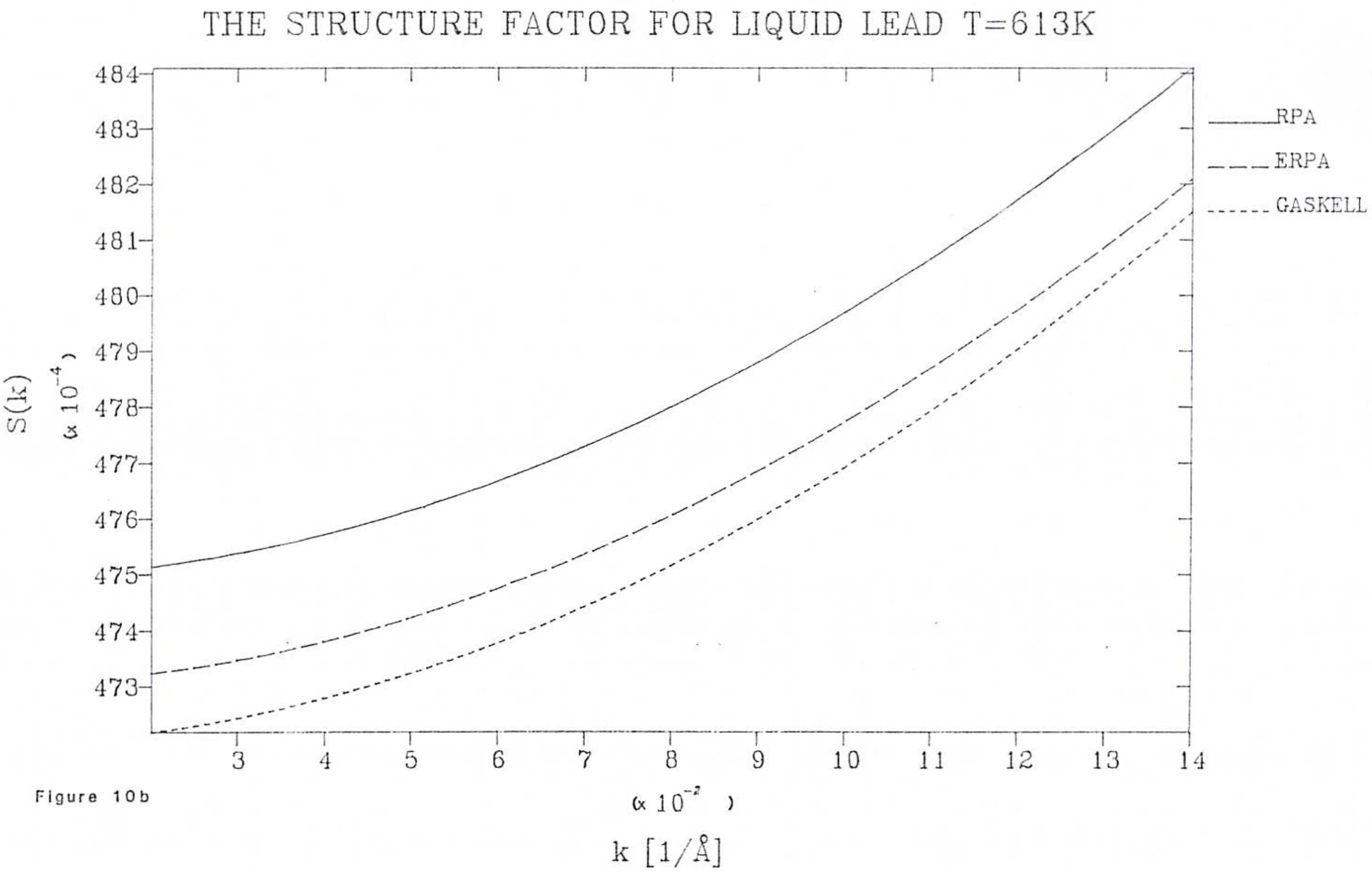

THE STRUCTURE FACTOR FOR LIQUID LEAD T=613K
S(k)
(x 10⁻⁴)
484
483
482
481
480
479
478
477
476
475
474
473
3
4
5
6
7
8
9
10
11
12
13
14
(x 10⁻²)
k [1/Å]
RPA
ERPA
GASKELL

Figure 10b

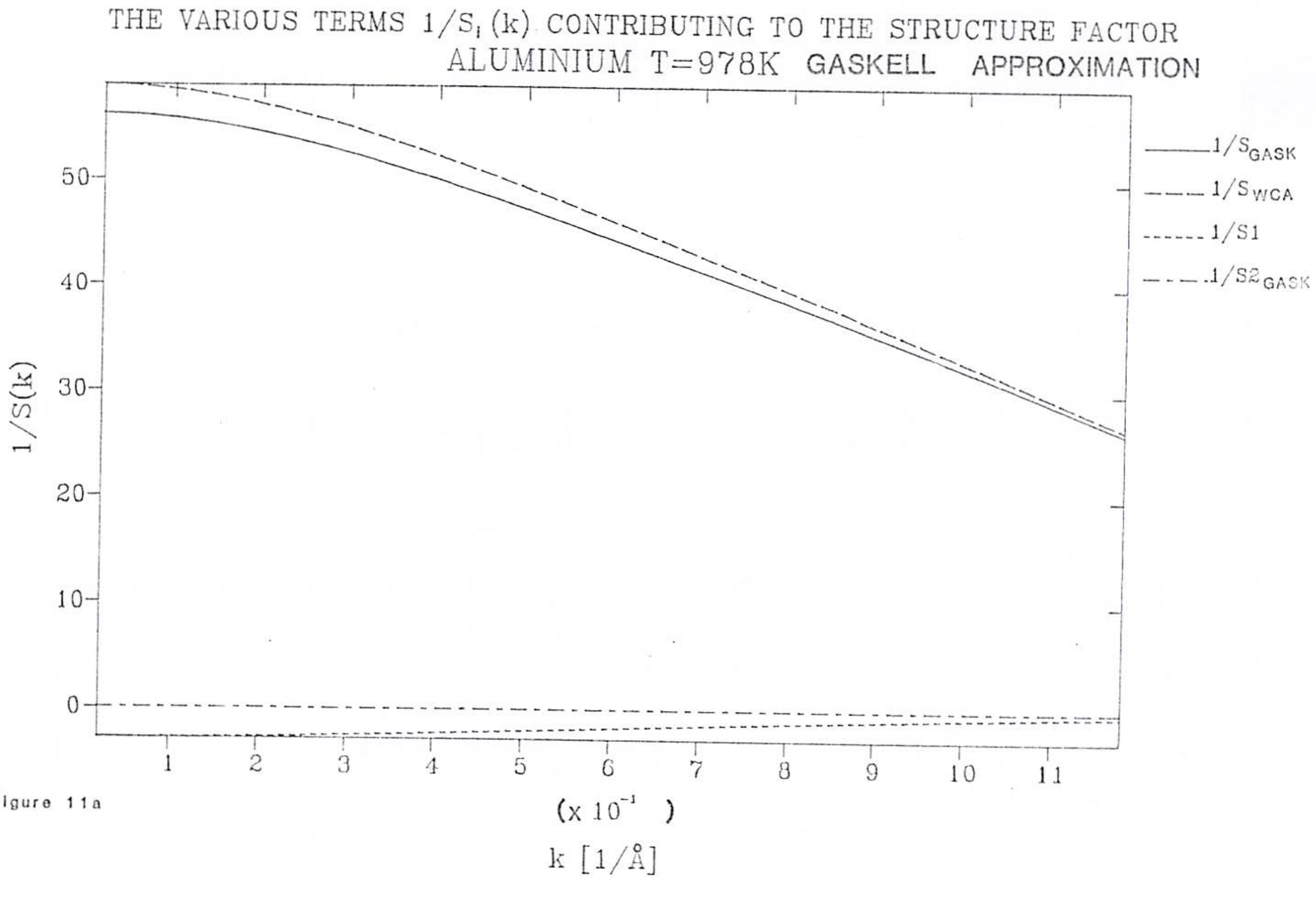

THE VARIOUS TERMS $1/S_i(k)$ CONTRIBUTING TO THE STRUCTURE FACTOR
ALUMINIUM T=978K GASKELL APPROXIMATION
$1/S_{GASK}$
$1/S_{WCA}$
$1/S1$
$1/S2_{GASK}$
1/S(k)
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
(x 10^{-1})
k [1/Å]

Figure 11a

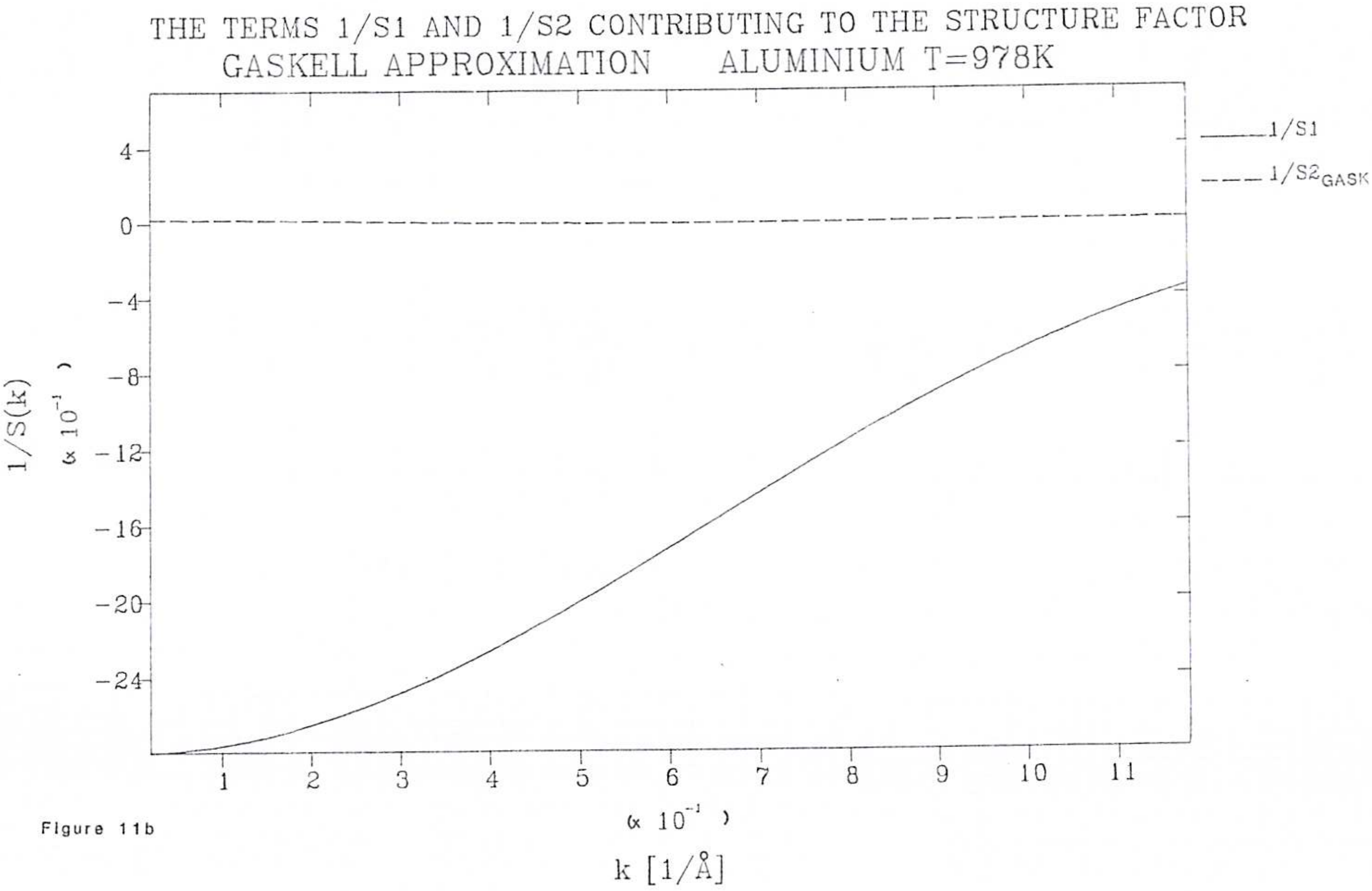
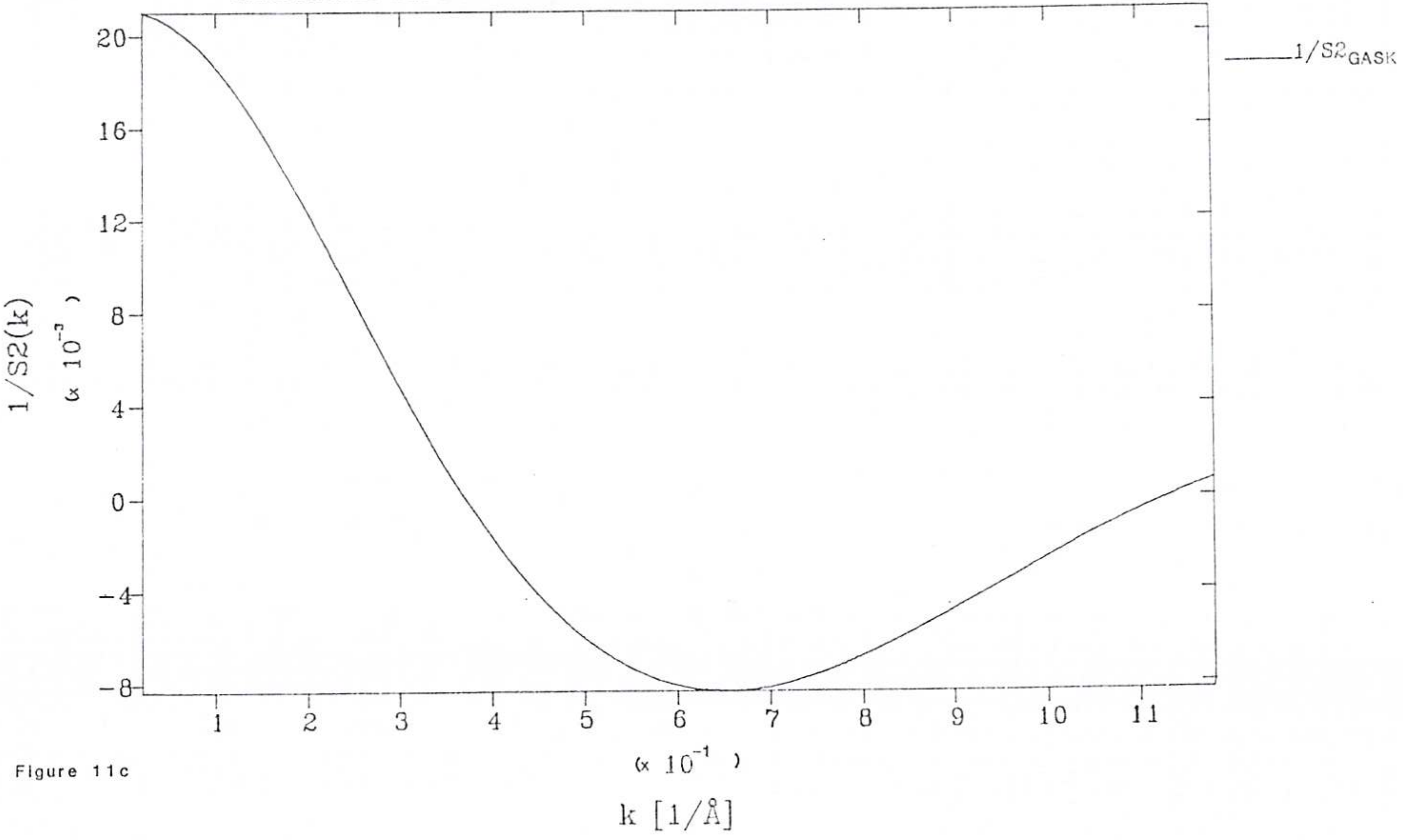

THE TERMS 1/S1 AND 1/S2 CONTRIBUTING TO THE STRUCTURE FACTOR
GASKELL APPROXIMATION ALUMINIUM T=978K
1/S1
1/S2GASK
4
0
-4
-8
-12
-16
-20
-24
1/S(k)
(x 10⁻¹)
1
2
3
4
5
6
7
8
9
10
11
(x 10⁻¹)
k [1/Å]

Figure 11b



THE TERM 1/S2(k) CONTRIBUTING TO THE STRUCTURE FACTOR
GASKELL APPROXIMATION   ALUMINIUM T=978K

Figure 11c

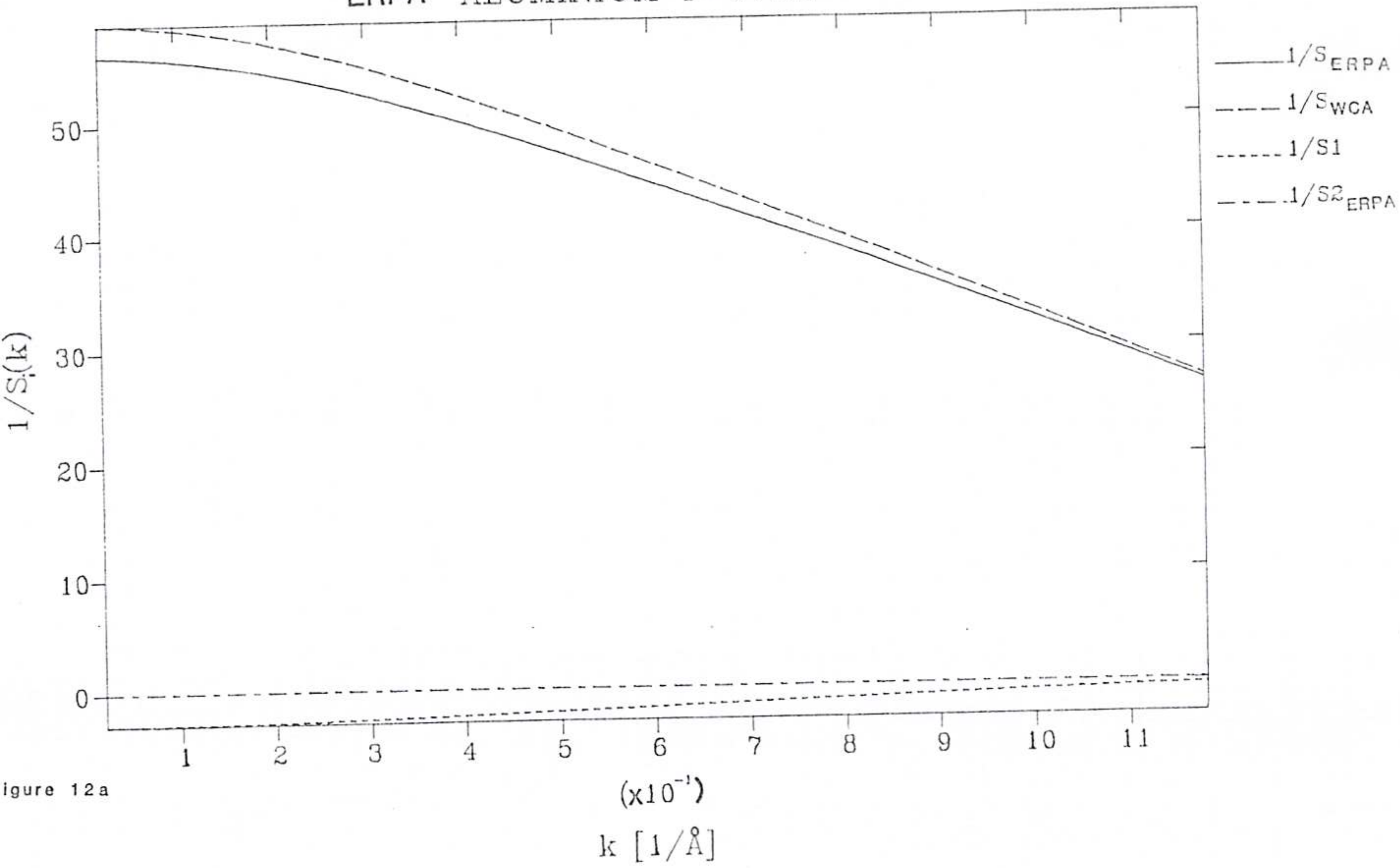

THE VARIOUS TERMS $1/S_i(k)$ CONTRIBUTING TO THE STRUCTURE FACTOR
ERPA ALUMINIUM T=978K

Figure 12a

THE TERMS $1/S1(k)$ AND $1/S2(k)$ CONTRIBUTING TO THE STRUCTURE FACTOR
ERPA ALUMINIUM T=978K

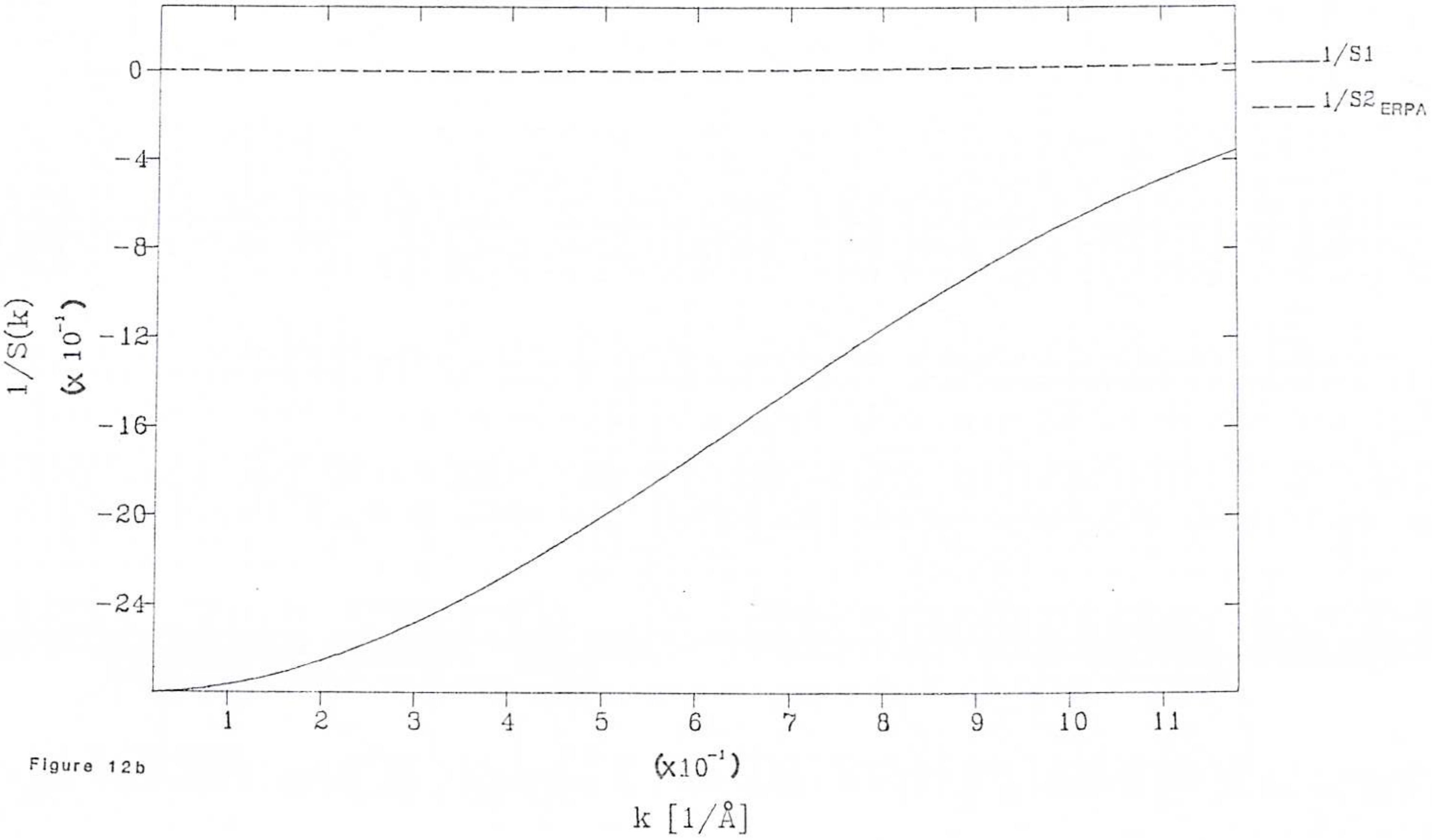


Figure 12b

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THE TERM 1/S2(k) CONTRIBUTING TO THE STRUCTURE FACTOR
ERPA ALUMINIUM T=978K

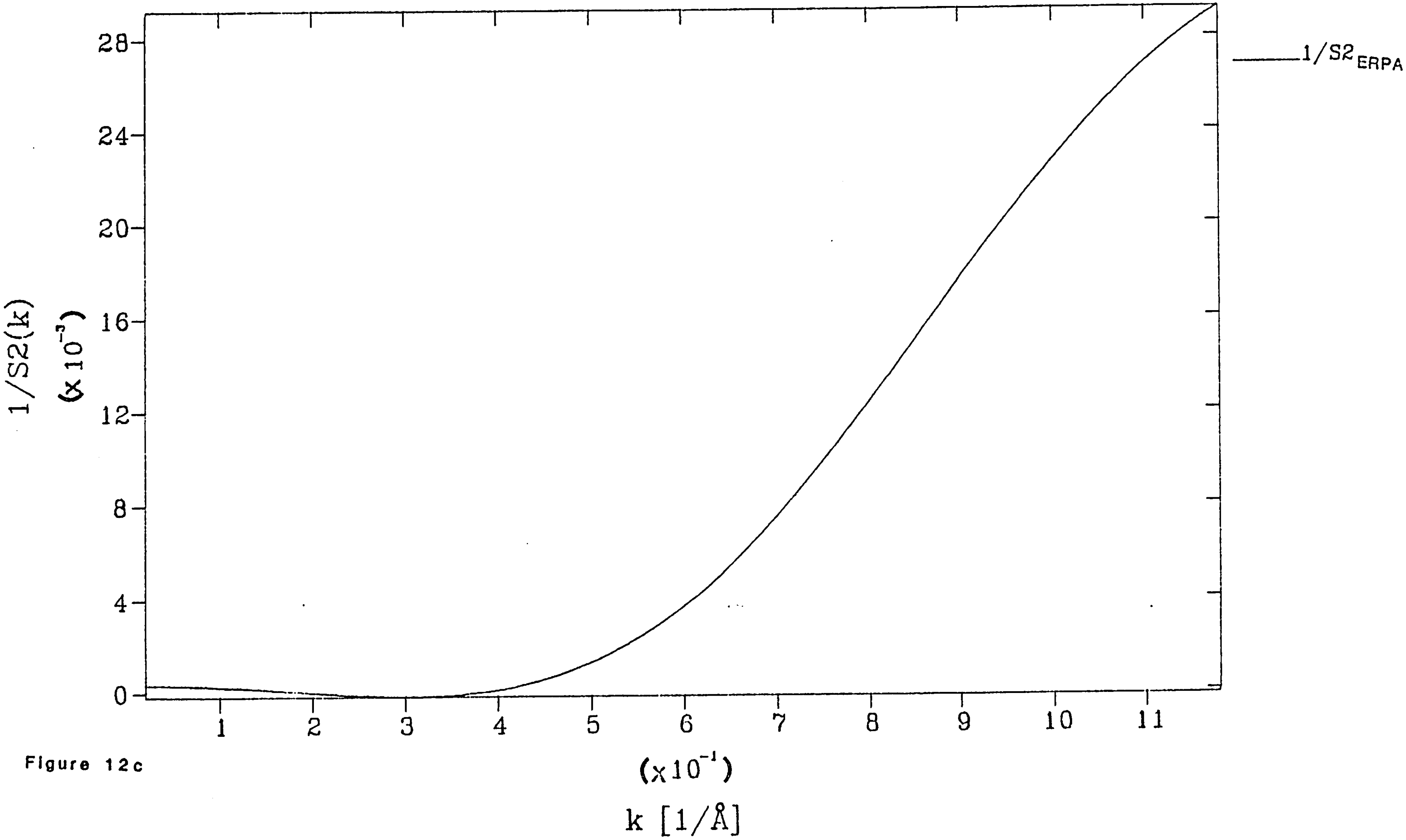

Figure 12c

THE VARIOUS TERMS $1/S_i(k)$ CONTRIBUTING TO THE STRUCTURE FACTOR
GASKELL APPROXIMATION ALUMINIUM T=943K

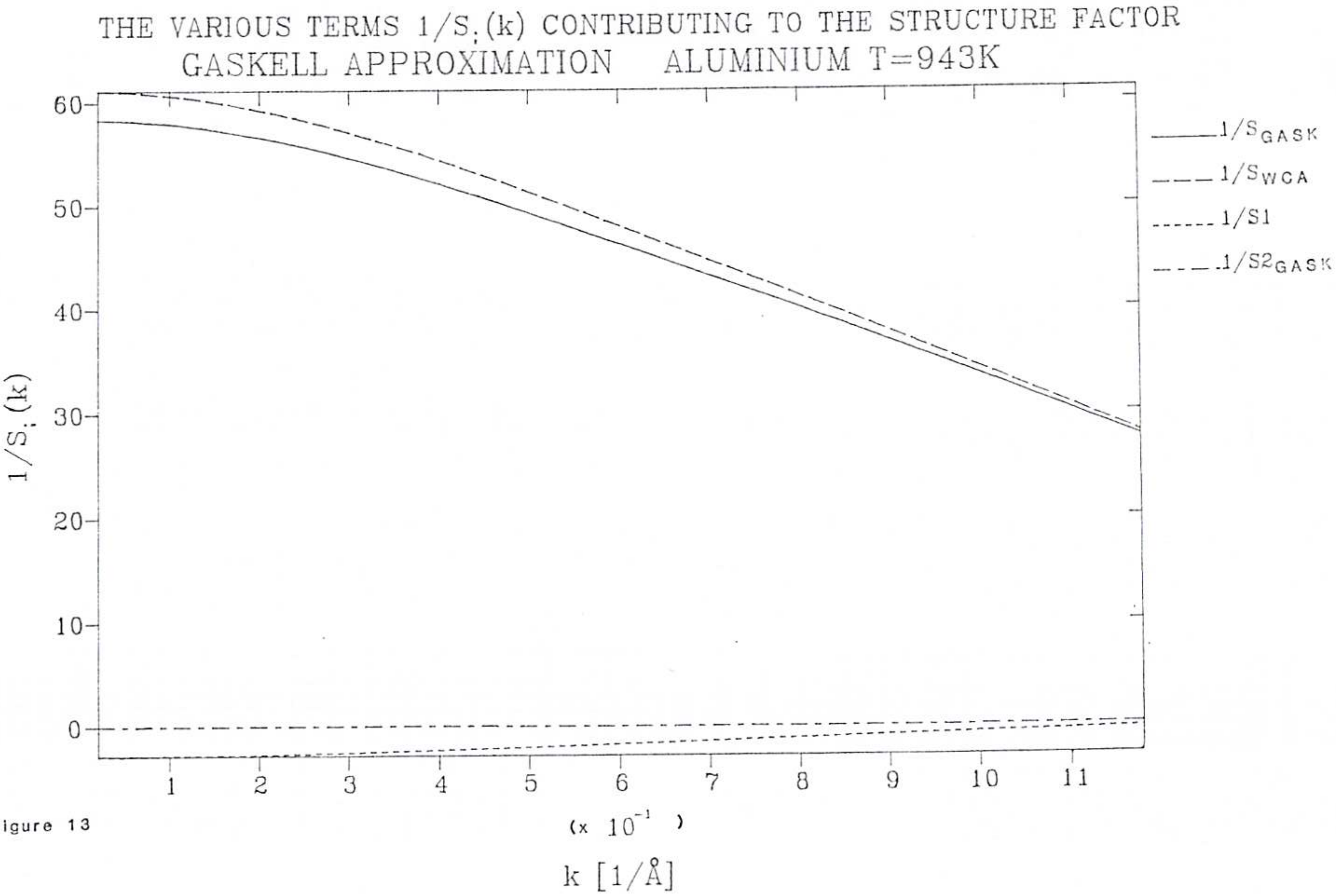

Figure 13

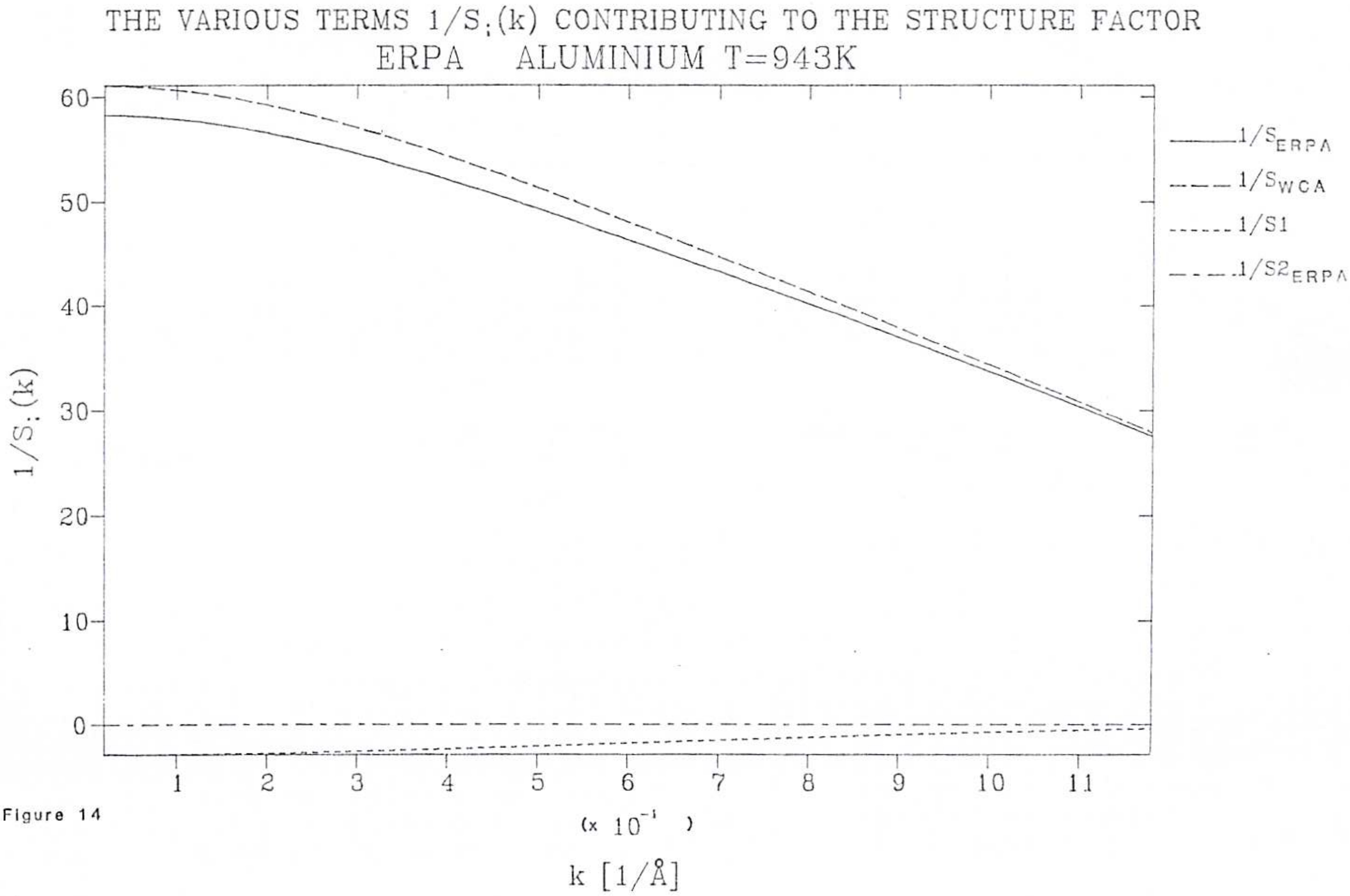
THE VARIOUS TERMS $1/S_i(k)$ CONTRIBUTING TO THE STRUCTURE FACTOR
ERPA ALUMINIUM T=943K
$1/S_i(k)$
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
(x 10^{-1})
k [1/Å]
$1/S_{ERPA}$
$1/S_{WCA}$
$1/S1$
$1/S2_{ERPA}$

Figure 14