

STATISTICAL MECHANICS OF LIQUIDS

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THE present review deals exclusively with the closed nonlinear integral equation of Percus and Yevick (PY). Equally powerful and also closed is the well-known hypernetted chain equation (HNC). The former integral equation however has been solved analytically for the hard sphere potential and with the aid of perturbation theories of liquids one can obtain thermodynamic properties even with attractive potential tails with the hard sphere potential solution as a reference system.

The most important property of liquids is the experimentally measurable structure function (SF) which can be determined either by x-ray or neutron diffraction. There are methods¹ and improvisations^{2,3} in the theoretical calculations of SF. The first set of calculations of SF were made with hard sphere potential by Ashcroft and Lekner¹ and its evaluation with an attractive tail in the random phase approximation (RPA) was extensively investigated by the author and his co-workers⁴⁻⁸.

ATOMIC LIQUIDS

In the case of atomic liquids the evaluation of the SF is simple and one is not confronted with the orientational problems. Thus as is well-known the structure function is obtained through the following equation.

$$S(K) = \frac{1}{1 - \rho \tilde{c}(K)} \quad (1)$$

Here ρ is the number density and $\tilde{c}(K)$ is the Fourier transform (FT) of the well-known direct correlation function (DCF). In the evaluation of the SF in the RPA we use the following established perturbation approximation. Thus the DCF is approximated as

$$C(r) = C_{hs}(r) \quad \Omega \leq \sigma \quad (2)$$

$$= -U(r)/k_B T \quad \Omega > \sigma \quad (3)$$

The third equation is known as the mean spherical model approximation (MSMA). Here $C_{hs}(r)$ is the hard sphere direct correlation function obtained by Wertheim and Theiele (WT) from the PY equation. $U(r)$ is the potential function and k_B is the Boltzmann's constant. For a square well potential we have

$$U(r) = \begin{cases} \infty & r \leq \sigma \\ -\epsilon & \sigma < r \leq \lambda \sigma \\ 0 & r > \lambda \sigma \end{cases} \quad (4)$$

Here the symbols have their usual significance. The W-T solution of the DCF can be written as:

$$C(r) = -\frac{1}{(1-\eta)^4} \left[(1+2\eta)^2 - 6\eta \left(1 + \frac{\eta}{2}\right) \left(\frac{r}{\sigma}\right) + \frac{\eta}{2} (1+2\eta)^2 \left(\frac{r}{\sigma}\right)^3 \right] \quad (5)$$

where η is the packing fraction and is defined through the equation

$$\eta = \pi \rho \sigma^3 / 6 \quad (6)$$

Here σ is the so-called collision diameter. From (4) and (5) one can immediately obtain the SF through a proper choice of the potential parameters⁴⁻¹⁰.

When once the structure factor is known one can immediately obtain the radial distribution function (RDF) by the FT of SF. Thus the RDF and SF are related by

$$h(r) \equiv g(r) - 1 = -\frac{1}{(2\pi)^3} \int_0^\infty [S(K) - 1] \exp(i\vec{K} \cdot \vec{r}) dK \quad (7)$$

Here $h(r)$ is known as the total correlation function. We present below some typical SF's calculated in the RPA^{2,3}.

The importance of the theoretical evaluation of the SF can be assessed from the fact that it enables one to formulate the equation of state in the long wave limit. Thus the equation of state in the RPA for square well fluids¹¹ and the Lennard-Jones (L-J) fluids¹² can be written respectively as

$$\frac{PV}{RT} = \frac{1+\eta+\eta^2}{(1-\eta)^3} - \frac{4\epsilon\eta(\lambda^3-1)}{k_B T} \quad (8)$$

$$\text{and } \frac{PV}{RT} = \frac{1+\eta+\eta^2}{(1-\eta)^3} - \frac{32\epsilon\eta}{3k_B T} \quad (9)$$

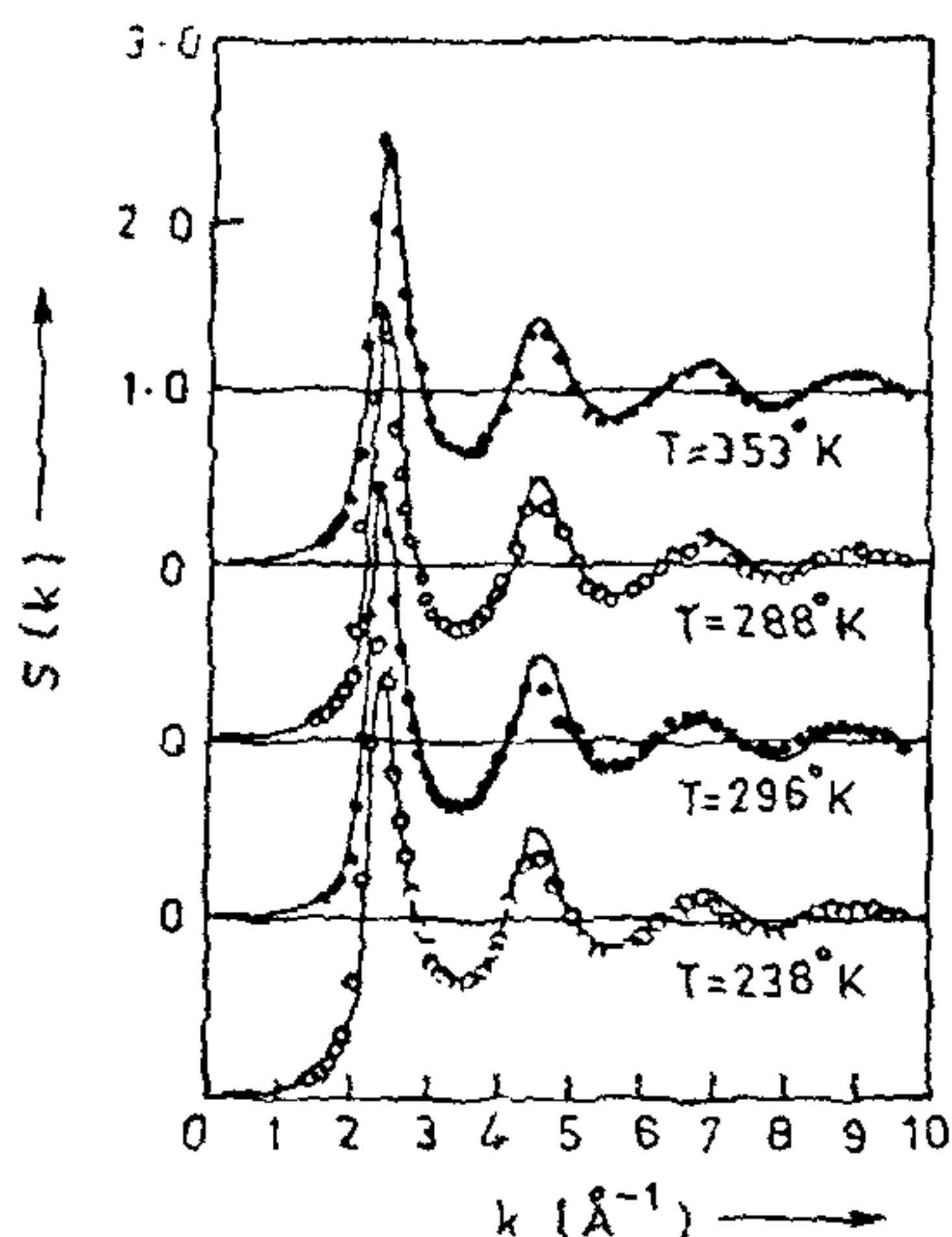


Figure 1. Structure factor of Liquid mercury calculated values (—) experimental values (ooo and ●●●).

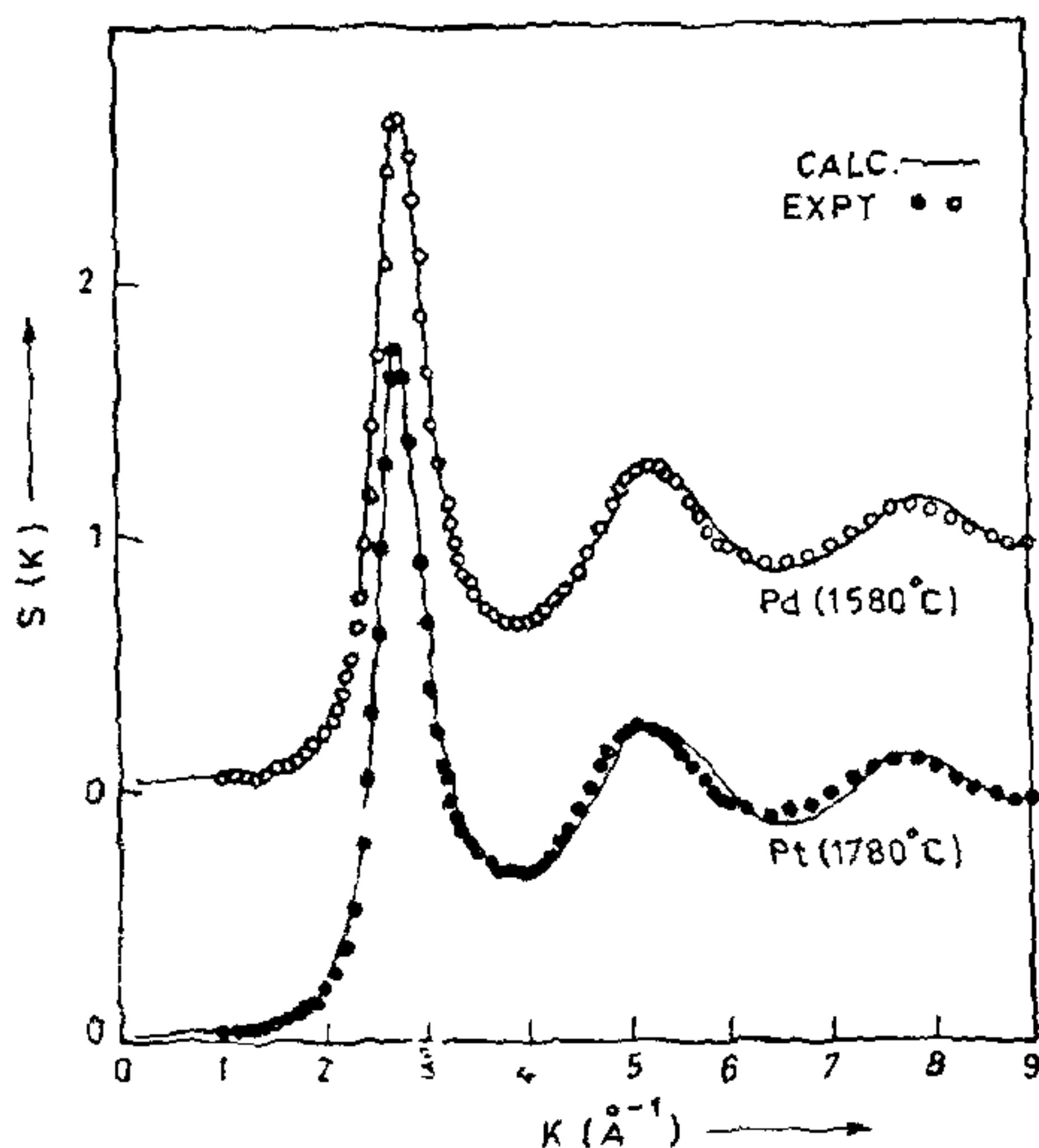


Figure 2. Structure factor of Liquid palladium and platinum—calculated values (—) experimental values (ooo and ●●●).

where the parameters have their usual significance.

From the above equations several thermodynamic properties of the liquids can be calculated and these are found to be, in many cases, in fair

agreement with experiment. The equation of state so developed can also be used to evaluate acoustic properties¹³ nonlinear acoustic parameters¹³ and elastic constants^{14,15}. The various methods used to compute these properties have not been described due to space considerations.

Partial Structure function of Alloys:

The SF calculations can be extended to alloys in the Ashcroft-Langreth model using the MSMA^{16,17}.

It is also possible to calculate the transport properties from the SF either through Helfand prescription¹⁸ or through David-Luks-Singers approximation¹⁹. Thus a whole range of properties of liquids can be calculated from the SF.

A Method of Evaluation of the Potential function from SF:

One of the fundamental properties of matter is the evaluation of the potential function governing the molecules in liquids. Rao and Joardar derived this from the requirement that an exact theory of the RDF must produce the same result either in the evaluation of pressure or compressibility. They showed that²⁰

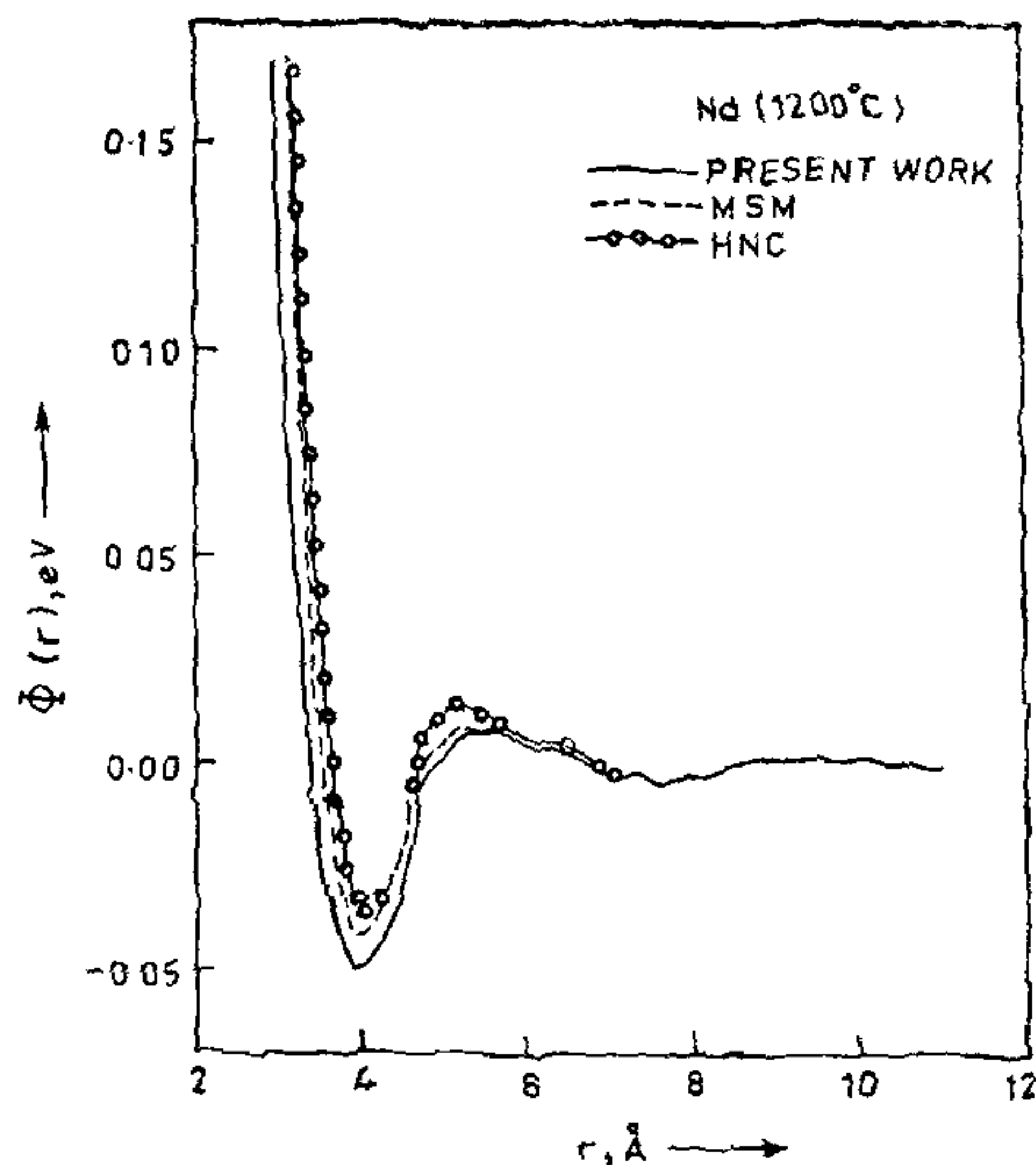


Figure 3. Interionic pair potential of Nd (1200°C) calculated from equation 10 (—) MSMA (....) and HNC (o-o-o).

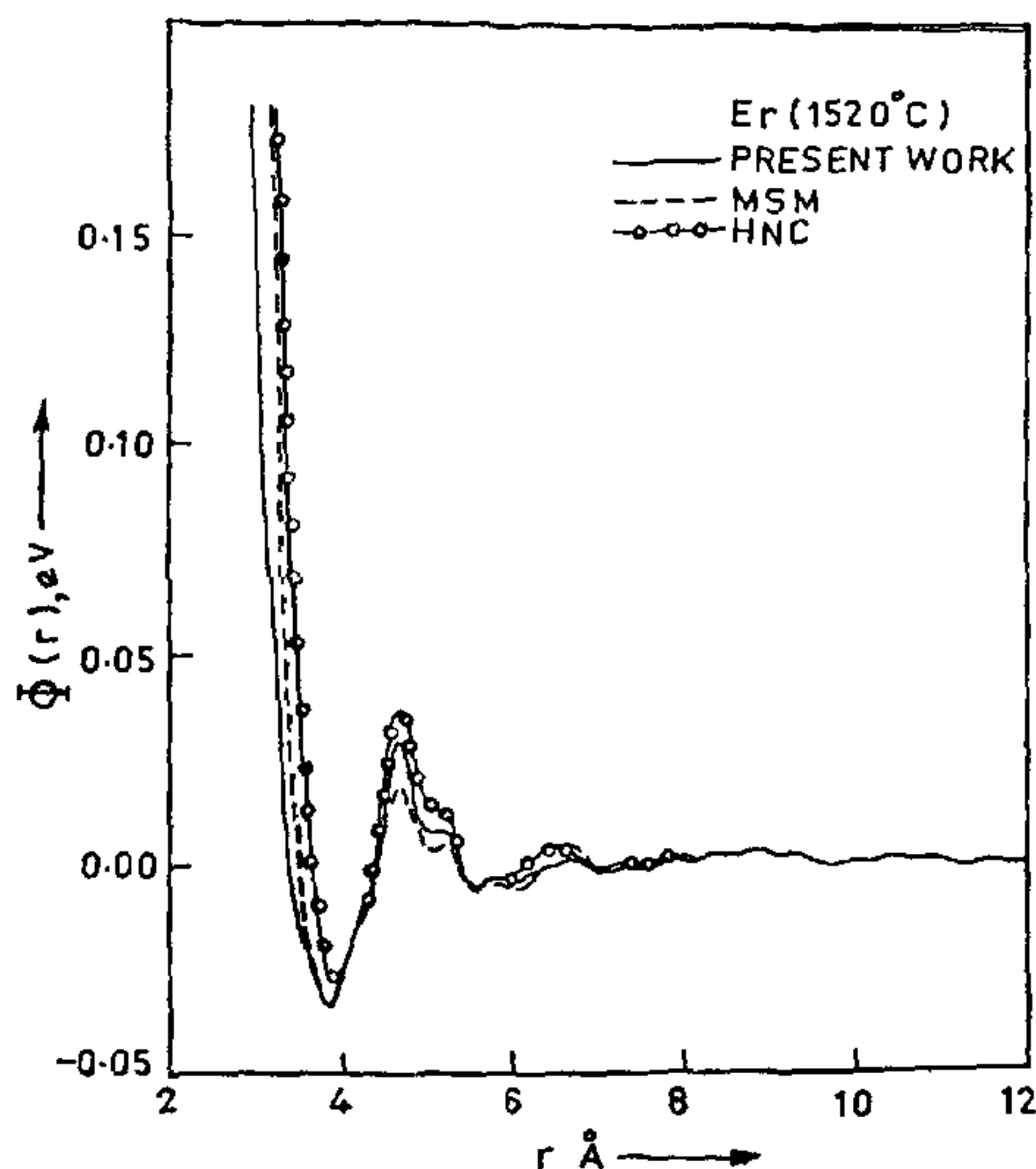


Figure 4. Interionic pair potential of Er (1520°C) calculated from equation 10 (—) NSMA (.....) and HNC (—o—o—o—).

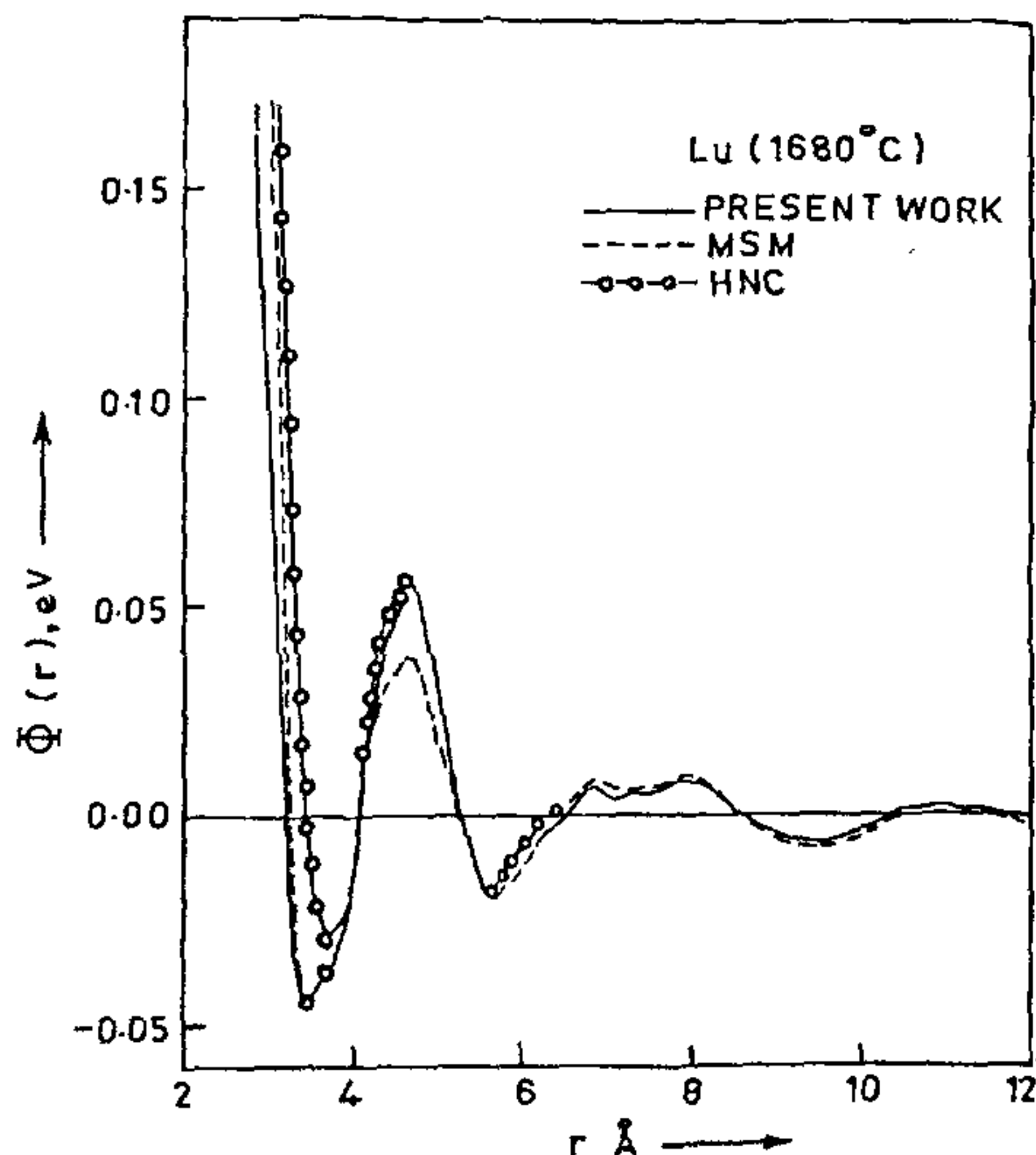


Figure 5. Interionic pair potential of Lu (1680°C) calculated from equation 10 (—) MSMA (.....) and HNC (—o—o—o—).

$$\beta U(r) = \frac{1}{2\pi^2\rho} \int_r^\infty \left\{ \left[\frac{1}{r'^2} \int_0^\infty K \left(\frac{S(K)-1}{S(K)} \right) \times \left(Kr' \cos Kr' - \sin Kr' \right) dK \right] \left[1 + \frac{1}{2\pi^2\rho r'} \int_0^\infty (S(K)-1) K \sin Kr' dK \right] \right\} dr' \quad (10)$$

We present below the interionic potential of some of the rare earth metals²¹.

Higher order distribution functions:

Egelstaff *et al.* proposed a method of determining triplet and quadruplet correlation functions through the isothermal pressure derivatives of $S(K)$. $g_3(r, s)$ has also been evaluated by means of Monte-Carlo (MC) and molecular dynamics (MD) computations for hard spheres²² and for L-J system²³ respectively.

The isothermal pressure derivatives of SF in the model $\rho^{1/3}$ are given by

$$\rho K_B T \left[\frac{\partial S(K)}{\partial \rho} \right]_T = - \frac{K}{3} S^2(0) \left[\frac{\partial S(K)}{\partial K} \right]_T \quad (11)$$

$$(\rho K_B T)^2 \left(\frac{\partial^2 S}{\partial \rho^2} \right)_T = \frac{K}{9} S^2(0) \times \left[4 \frac{\partial S(K)}{\partial K} + K \frac{\partial^2 S(K)}{\partial K^2} \right]_T \quad (12)$$

The expressions for $[\partial S(K)/\partial K]_T$ and $[\partial^2 S(K)/\partial K^2]_T$ were evaluated by Rao and Murty^{24,25} in the RPA and the expressions being lengthy have not been given here and may be found in the original papers. We produce below the isothermal pressure derivatives of Hg, Na and Rb.

Perturbation Theories of Liquids and the evaluation of Thermodynamic properties:

Barker and Henderson successfully explained²⁶ the behaviour of square well fluids through a perturbation of the attractive tail over the hard sphere potential. The expression they obtained for the Helmholtz free energy through the so-called local compressibility approximation can be written as follows

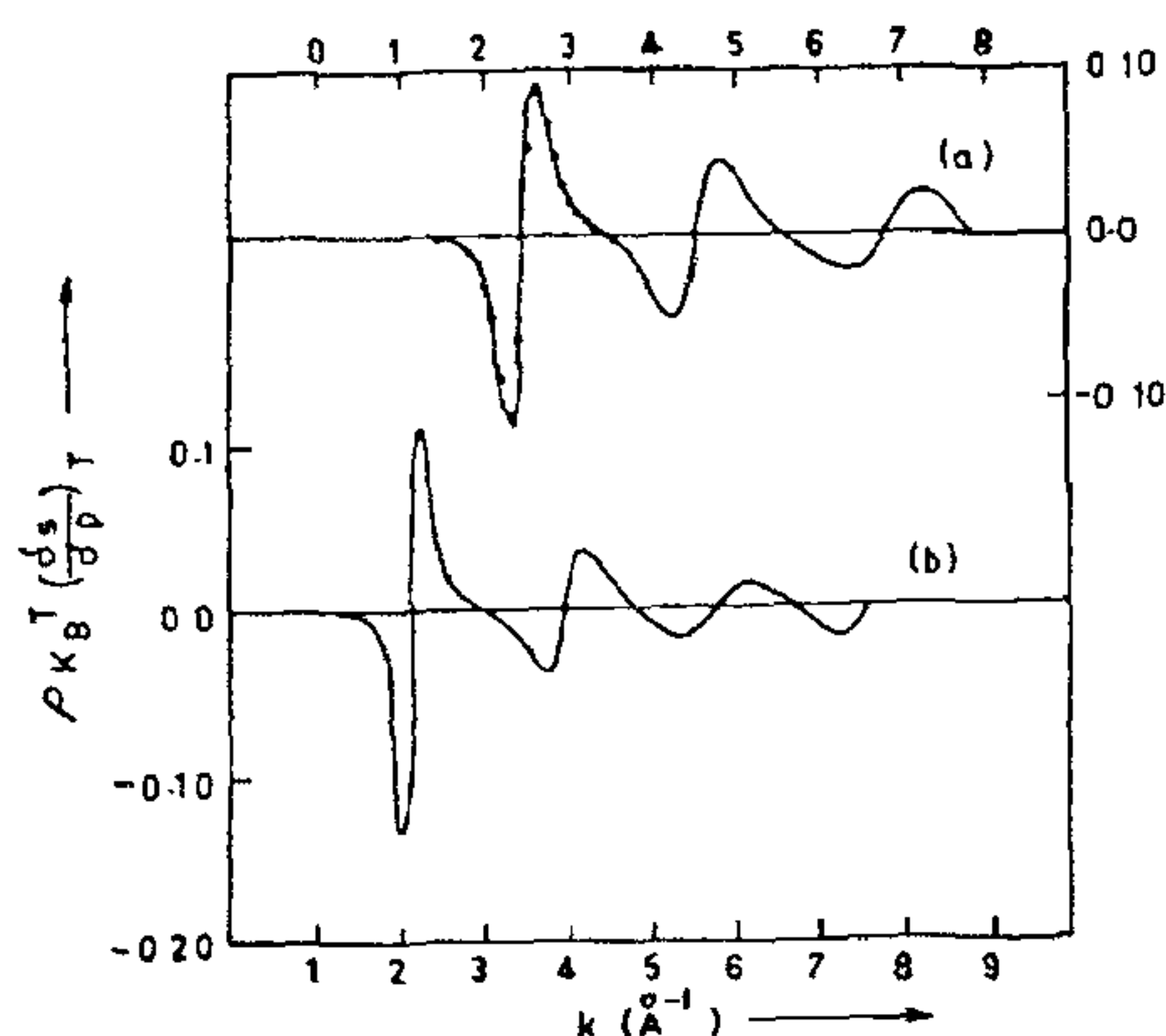


Figure 6. The isothermal pressure derivatives of $S(K)$: (a) Mercury at $T=294.9\text{K}$ and $P=2\text{K bar}$ (full line) and $P=12\text{K bars}$ (full circles), (b) sodium at $T=373$ and $P=5\text{K bars}$.

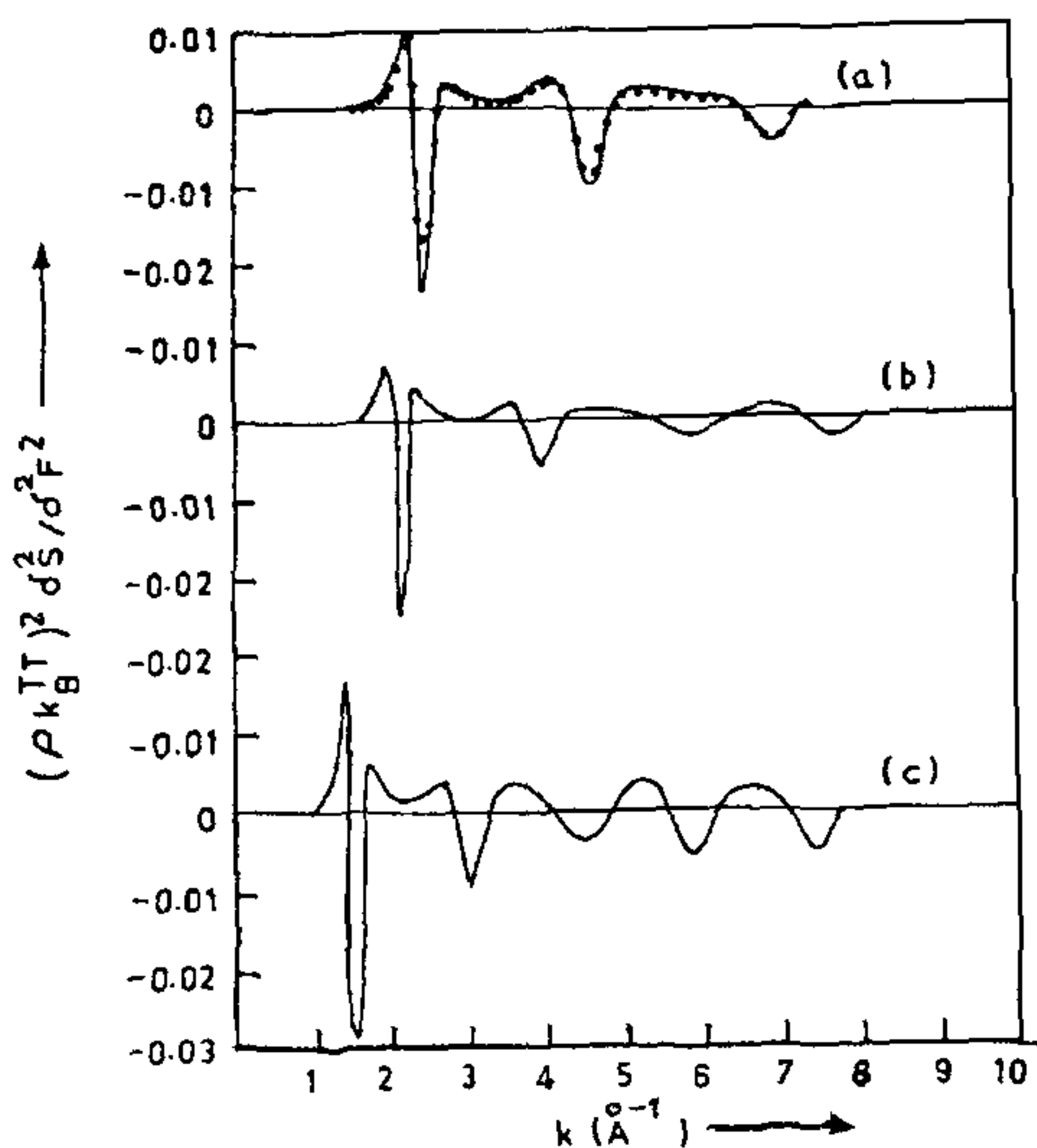


Figure 7. The isothermal second pressure derivative of $S(K)$ for cases a and b listed in figure 6. Rubidium at $T=333\text{K}$ and $P=0.43\text{K bars}$.

The expressions for $\left[\frac{\partial S(K)}{\partial K} \right]_T$ and $\left[\frac{\partial^2 S(K)}{\partial K^2} \right]_T$

$$\frac{A-A_0}{N k_B T} = -2\pi\rho \left(\frac{\epsilon}{K_B T} \right) \frac{\lambda\sigma}{\sigma} \int_{\sigma}^{\infty} r^2 g_0(r) dr - \pi\rho \times \left(\frac{\epsilon}{K_B T} \right)^2 \frac{(1-\eta)^4}{1+4\eta+4\eta^2} \times \frac{\partial}{\partial \rho} \times \left[\rho \int_{\sigma}^{\infty} r^2 g_0(r) dr \right] \quad (13)$$

Here $g_0(r)$ is the well-known hard sphere RDF and the rest of the symbols have their usual significance. Barker and Henderson obtained the pressure and the critical constants through numerical differentiation of the above equation.

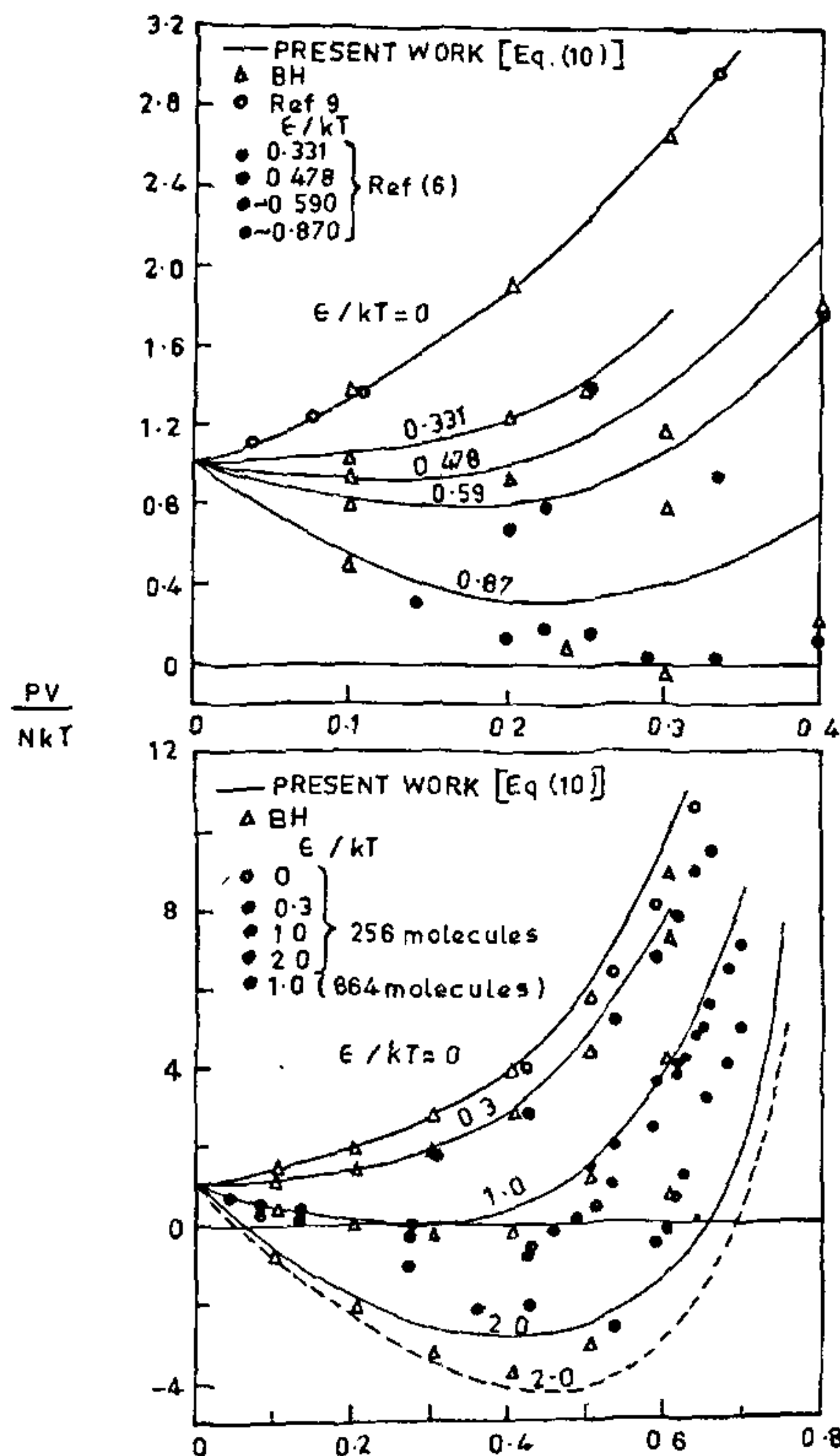


Figure 8. Equation of state obtained through equation (10) of reference 27 with low ϵ/KT values.

Figure 9. Equation of state obtained through equation (10) of reference 27 with higher values of ϵ/KT .

However Rao and Nammalvar²⁷ using the compressibility equation of state and assuming that $g(r) = 1$ for $r > \lambda$ obtained analytical expressions for the pressure, compressibility and $C_1 \equiv [\partial(1/\beta)/\partial p]_T$. The isotherms obtained by Rao and Nammalvar agree well with those obtained by MC and MD results. Their results are shown in figures 8 and 9.

Swamy and Wankhede²⁸ gave analytical expressions for the Helmholtz free energy of a triangular well fluid in the Barker-Henderson perturbation approximation.

The Pseudopotential study of Liquid Metals:

The Pseudopotential is defined through the equation

$$W(r) = V(r) + \left[E_K + \frac{\hbar^2 \nabla^2}{2m_e} - V(r) \right] P \quad (14)$$

where P is the projection operator and is given by $P = \sum_{\alpha} |\alpha\rangle \langle \alpha|$ and $|\alpha\rangle$ is the single core electron Wave function which are orthogonal to the conduction band electrons that are free to move and are given by the wave function Ψ_K and is in general a linear combination of OPW's (orthogonal plane waves).

The first order perturbation expression for the interaction between an electron and a system of ions can be written in terms of the so-called "plane wave matrix elements" and they turn out to be independent of the wave vector K and are the FT of $W(r)$; the pseudopotential. It can be easily found out that the matrix elements is a product of the geometric structure function and the screened ion form factor. This can be written as:

$$\langle K+q|W|K\rangle = S(q) \tilde{W}(q), \quad (15)$$

$$\text{where } S(q) = \frac{1}{N} \sum_j \exp(-iq \cdot r_j), \quad (16)$$

$$\text{and } \tilde{W}(q) = \frac{1}{\Omega} \int W(r-r_j) \times \exp[-iq \cdot (r-r_j)] dT \quad (17)$$

$$W(r) = \sum_j W(r-r_j) \quad (18)$$

Hence the effective atom-atom potential can be written as

$$\phi(r) = \frac{Z^{*2}e^2}{n} - \frac{2Z^{*2}e^2}{r} \int_0^\infty F_N(K) \times \frac{\sin Kr}{Kr} dK \quad (19)$$

where $F_N(K)$ is the normalised energy wave number characteristic given by

$$F(K) = \frac{2\pi Z^{*2}e^2}{rK^2} F_N(K) \quad (20)$$

While the function $F(K)$ is related to the pseudo-potential $W^0(K)$ by the equation

$$F(K) = \frac{\Omega K^2}{8\pi e^2} \left\{ \frac{1}{\epsilon(K)} - 1 \right\} \left| W^0(K) \right|^2 \quad (21)$$

$$W^0(K) = W(K) \epsilon(K) \quad (22)$$

Here Ω is the volume per atom, $W(k)$ is the FT of the unscreened pseudopotential, $\epsilon(K)$ is the dielectric response function and is related to the Hartree dielectric function ϵ^H as

$$\epsilon(q) = 1 + [1-f(q)] [\epsilon^H(q)-1] \quad (23)$$

$$\text{with } \epsilon^H(K) = 1 + \frac{2mK_F e^2}{\pi \hbar^2 k^2}$$

$$\times \left[1 + \frac{4K^2 - q^2}{4K_F K} \ln \frac{2K_F + K}{2K_F - K} \right] \quad (24)$$

In (23) the function $f(q)$ takes into account the exchange and correlation effects. There are several forms of this function but the one that is convenient to use is that due to Singwi *et al*²⁹. In metals like noble metals one has also to consider the overlap energy of the d state electrons. Hence (19) has to be modified to include the overlap forces. Thus the effective pair potential is given by

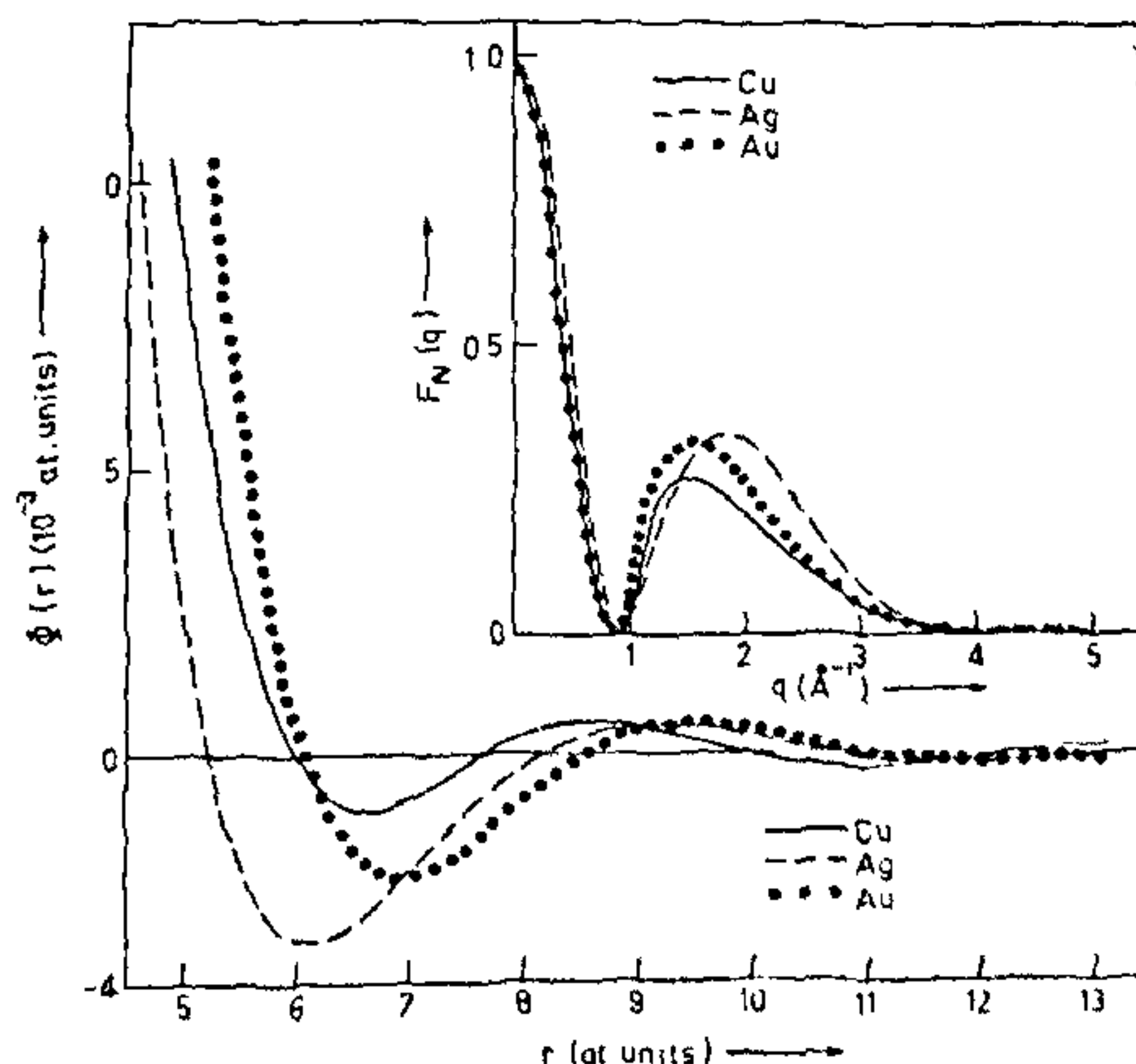


Figure 10. Effective pair potential for Cu, Ag and Au; Cu (—), Ag (---) and Au (....). Inset $F_N(q)$, the normalised energy wave number characteristic Cu (—), Ag (---) and Au (....).

$$\psi(r) = \frac{Z^2 e^2}{r} - \frac{2Z^2 e^2}{\pi} \int_0^\infty F_N(K) \frac{\sin kr}{kr} dk + V_{\text{ext}} \quad (25)$$

The potential so obtained³⁰ for Cu, Ag and Au are given in (figure 10). In addition one may obtain through variational technique using the Gibbs-Bogoliubov inequality both equilibrium and transport properties³⁰.

Molecular Liquids:

The study of molecular liquids poses a very difficult problem because of orientation of the molecules in the liquid state. There are two important approaches (1) orientational model (OM) approach and (2) the Reference Interaction Site Model (RISM) approach.

Oriental Approach: It was shown by Egelstaff³¹ that the molecular structure function can be written as

$$S_m(k) = f_1(k) + f_2(k) [S_c(K) - 1] \quad (26)$$

Here $S_m(k)$ is the molecular structure function, $f_1(k)$ is the molecular form factor while $f_2(k)$ also known as the form factor that depends upon the orientation of the molecules whereas the former depends entirely on the shape of a single molecule. $S_c(k)$ is known as the centre structure function. Using parallel and perpendicular orientations and a fraction parameter Rao and Joardar^{32,33} derived the molecular SF of CSe_2 ³² and nitrogen and O_2 ³³ and CS_2 ³⁴. In figure 11 we show the $S_m(K)$ of CS_2 . In polyatomic molecules it is necessary to assume some orientational model. Thus even for a big molecule like neopentane³⁵ and a pyramidal molecule like NH_3 ³⁶ one can derive the molecular SFS.

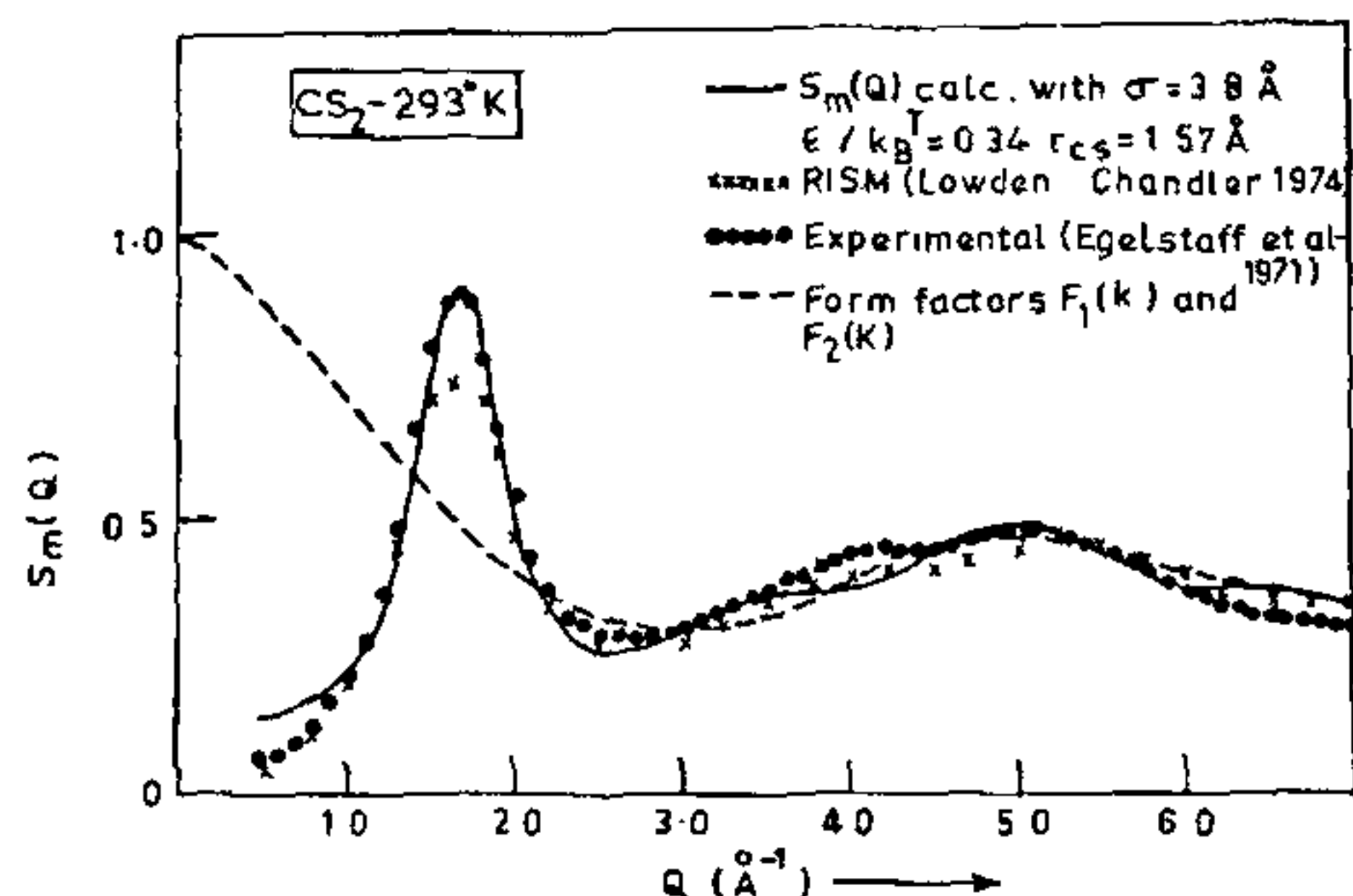


Figure 11. Molecular Structure factor $S_m(K)$ and form factors $f_1(K)$ and $f_2(K)$ of liquid CS_2 .

Reference interaction site model: In this theory³⁷ each molecule is assumed to have a specified number of interaction sites. The RISM equations relating to Site-Site total correlation function $h_{\alpha\gamma}(r)$ (TCF) to the Site-Site DCF $C_{\alpha\gamma}(r)$ and the Site-Site function $Y_{\alpha\gamma}(r)$ are written as

$$\hat{h}(K) = \hat{W}(K) \hat{C}(K) [I - \hat{W}(K) \hat{C}(K)]^{-1} \hat{W}(K) \quad (27)$$

$$C_{\alpha\gamma}(r) = \left\{ \exp[-U_{\alpha\gamma}(r)] - 1 \right\} Y_{\alpha\gamma}(r) \quad (28)$$

$$\text{and } h_{\alpha\gamma}(r) = Y_{\alpha\gamma}(r) + C_{\alpha\gamma}(r) - 1 \quad (29)$$

In the above equations, I is the unit matrix, ρ is the molecular number density and β is equal to $1/k_B T$. The function $U_{\alpha\gamma}(r)$ is the Site-Site interaction potential and the function

$$\hat{W}_{\alpha\gamma}(k) = \frac{\sin(k l_{\alpha\gamma})}{k l_{\alpha\gamma}} \quad (30)$$

where $l_{\alpha\gamma}$ is the distance between α and γ site. The function $W_{\alpha\gamma}(k)$ gives the ideal gas structure function for diatomic molecules and is equal to $1 + W_{\alpha\gamma}(K)$. The Site-Site pair distribution function $g_{\alpha\gamma}(r)$ is defined as:

$$g_{\alpha\gamma}(r) = h_{\alpha\gamma}(r) + 1 \quad (31)$$

The FT of $h_{\alpha\gamma}(r)$ is denoted by $h_{\alpha\gamma}(K)$. The RISM equations (27)–(29) can be solved numerically by a process of iteration³⁸ and the molecular structure function, $S_M(k)$ is related to $S(k)$ as

$$S_M(k) = \frac{\sum_{\alpha} \sigma_{\alpha}^2(k)}{[\sum_{\alpha} \sigma_{\alpha}(k)]^2} S(k) \quad (32)$$

while the structure function $S(k)$ for a RISM molecule with, say, four interaction sites as in the case of NH_3 is given by the relation:

$$S(k) = \left[\sum_{\alpha=1}^4 a_{\alpha}^2(k) \right]^{-1} \sum_{\alpha,\gamma=1}^4 a_{\alpha}(k) a_{\gamma}(k) \times [\hat{W}_{\alpha\gamma}(k) + \rho h_{\alpha\gamma}(k)] \quad (33)$$

Here $a_{\alpha}(k)$ stand for the x-ray scattering factor of the atom in which the α site is situated. In figure 12 we given the RISM structure function of liquid NH_3 obtained with hard sphere potential³⁹.

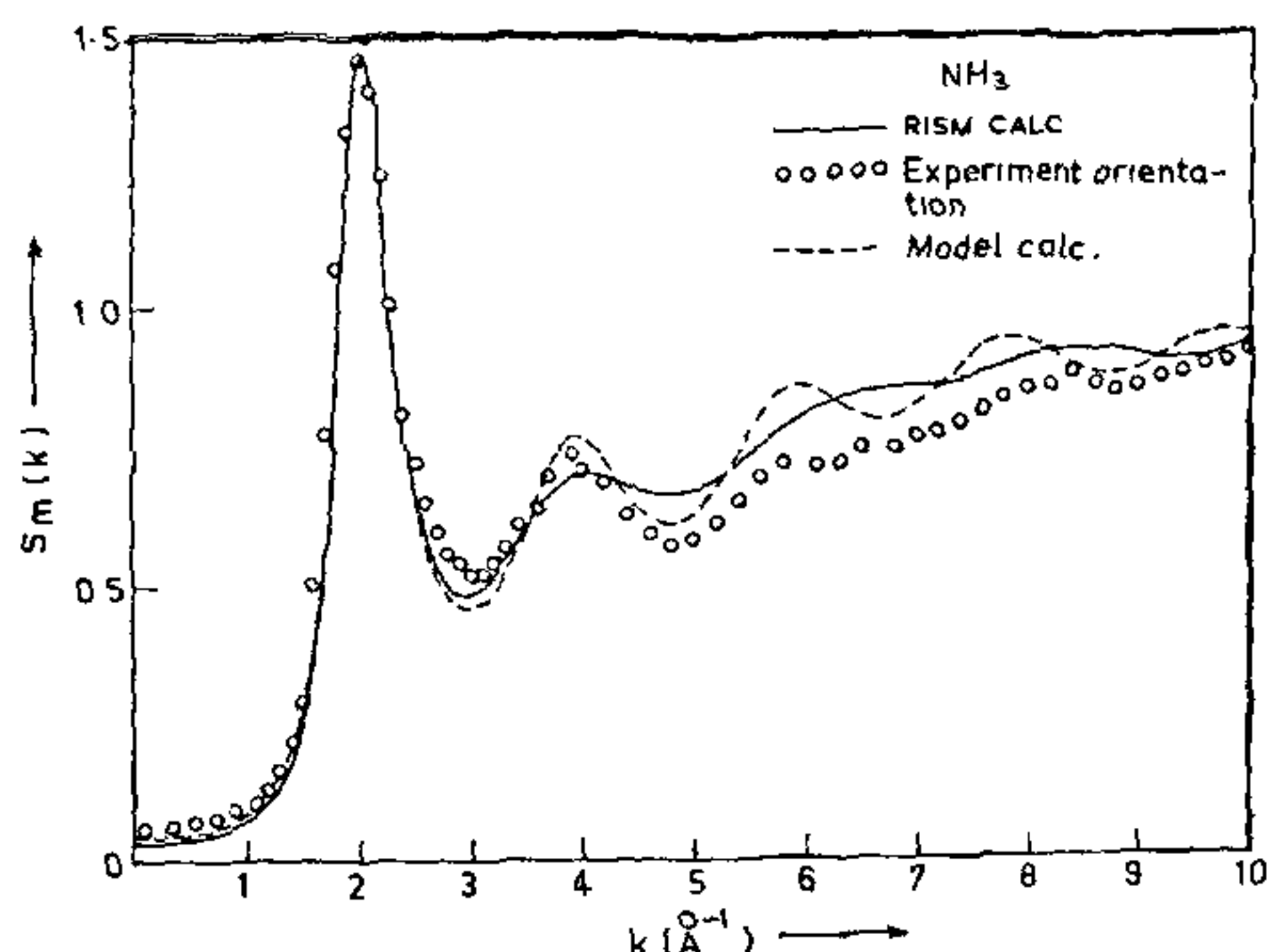


Figure 12. RISM molecular structure factor $S_m(K)$ of liquid NH_3 , RISM calculated values (—) experimental values (ooo) Model calculations (---).

It is not the aim of the author to give a detailed report of the various properties of liquids especially the transport properties of simple liquids, fused salts or electrolyte solutions in a short review like the present one where space limitations are an important factor to consider.

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