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WORKING PARTY

ON

"PHYSICS OF CONDENSED MATTER AT PLANETARY PRESSURES"

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LIQUID METALS - STRUCTURE

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Long-wavelength structure factors

From electroneutrality in liquid metal (as "alloy" of ions and electrons):

$$\begin{cases} -Ze = Ze\int d\underline{r}\; n_i\, g(r) - e\int d\underline{r}\; n_e\, g_{ie}(r) \\ +e = -e\int d\underline{r}\; n_e\, g_{ee}(r) + Ze\int d\underline{r}\; n_i\, g_{ie}(r) \end{cases}$$

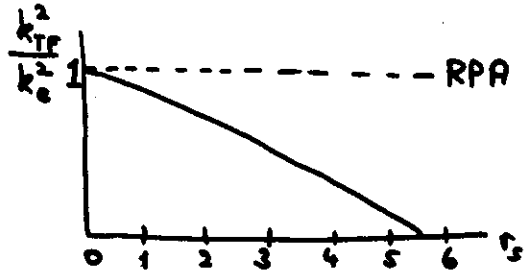
(Stillinger and Lovett 1968, Watabe and Hasegawa 1973, Chihara 1973)

$$\therefore \lim_{k\to 0}\left[Z^{-1} S_{ei}(k) = Z^{-1} S_{ee}(k) = S(k)\right]$$

$$= n_i k_B T K_T$$

Compressibility of liquid alkalis by long-waves method ($k\to 0$)

$$\varepsilon(k) \to 1 + \frac{k_e^2}{k^2} \qquad k_e^2 \propto K_e$$



$$\varepsilon_{OCP}(k) \to 1 + \frac{k_i^2}{k^2} \qquad k_i^2 \propto K_{OCP}$$

$$\therefore \quad S_{OCP}(k) \to \frac{k^2/k_D^2}{1 + k^2/k_i^2} \qquad k_D^2 = \frac{4\pi\rho e^2}{k_B T} \text{ (Debye-Hückel)}$$

k_i^2 strongly negative (strong ion-ion coupling!)

$k \to 0$

$$S(k) \to \frac{1}{\frac{k_D^2}{k_e^2} + \frac{k_D^2}{k_i^2} + k_D^2 R_c^2}$$

↑ take R_c from phonon curves of solid alkalis

		Na (200°C)	K (64°C)	Rb (39°C)	Cs (28°C)
K_T	th	18.7	39.3	53.1	68.2
	expt	19.9–20.8	38.2–41.9	49.5	62.7
$-\frac{\partial \epsilon}{\partial T}\Big\|_p$	th	0.69	0.56	0.40	0.38
	expt	0.52	0.53	~0.4	≈0.3

For liquid Na at 200°C:

$$S(k) \to \frac{1}{10 - 60 + 80} = 0.029 \quad \text{(expt. 0.032)}$$

↑ 40 in RPA!

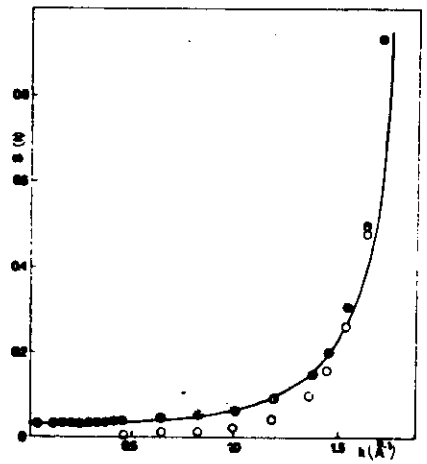


Fig. 99. Structure factor $S(k)$ of liquid sodium at 200°C in the small angle scattering region. The curve reports the X-ray data of A. J. Greenfield *et al.*[54], while the dots show the theoretical results obtained by screening the structure factor of the bare ionic plasma (shown by the circles).

LIQUID METAL ALLOYS: THERMODYNAMICS

$$\left.\begin{aligned} \rho(k,t) &\propto M_1 \rho_1(k,t) + M_2 \rho_2(k,t) \\ c(k,t) &\propto c_2 \rho_1(k,t) - c_1 \rho_2(k,t) \end{aligned}\right\} \rightarrow \text{matrix of structure factors}$$

Kirkwood and Buff (1951): for short range forces, thermodynamic properties of a two-component mixture are related to $\lim_{k\to 0}$ of structure factors:

$$\lim_{k\to 0}\left[S_{\rho\rho}(k),\ S_{cc}(k),\ S_{c\rho}(k)\right] \Rightarrow$$

$$\Rightarrow \left.\frac{\partial \mu_\alpha}{\partial \rho_\beta}\right|_{T,V,\rho_{\bar\beta}} \quad (\text{8 Hansen}) \qquad (\alpha,\beta: 1,2)$$

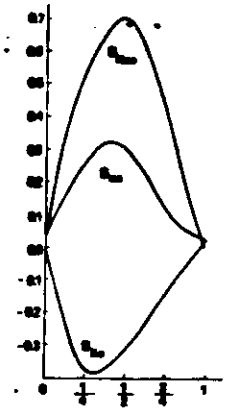
$$\Rightarrow \left[K_T,\ \frac{1}{V}\left.\frac{\partial V}{\partial c}\right|_{T,p},\ \left.\frac{\partial \mu_2}{\partial c}\right|_{T,p}\right]$$

$$\lim_{k\to 0} S_{cc}(k) = \frac{(1-c)k_B T}{\left(\partial P_2/\partial c\right)_{T,p}}$$

With electroneutrality:

$$\lim_{k\to 0}\left[S_{e_1}(k) = \left(\frac{n_1}{n_e}\right)^{1/2} Z_1 S_{11}(k) + \left(n_2/n_e\right)^{1/2} Z_2 S_{12}(k)\right]$$

(Bhatia et al (p73)



Concentration

Fig. 66. Electron–ion and electron–electron structure factors versus concentration in a liquid Na–K alloy. From N. H. March *et al.*[407]

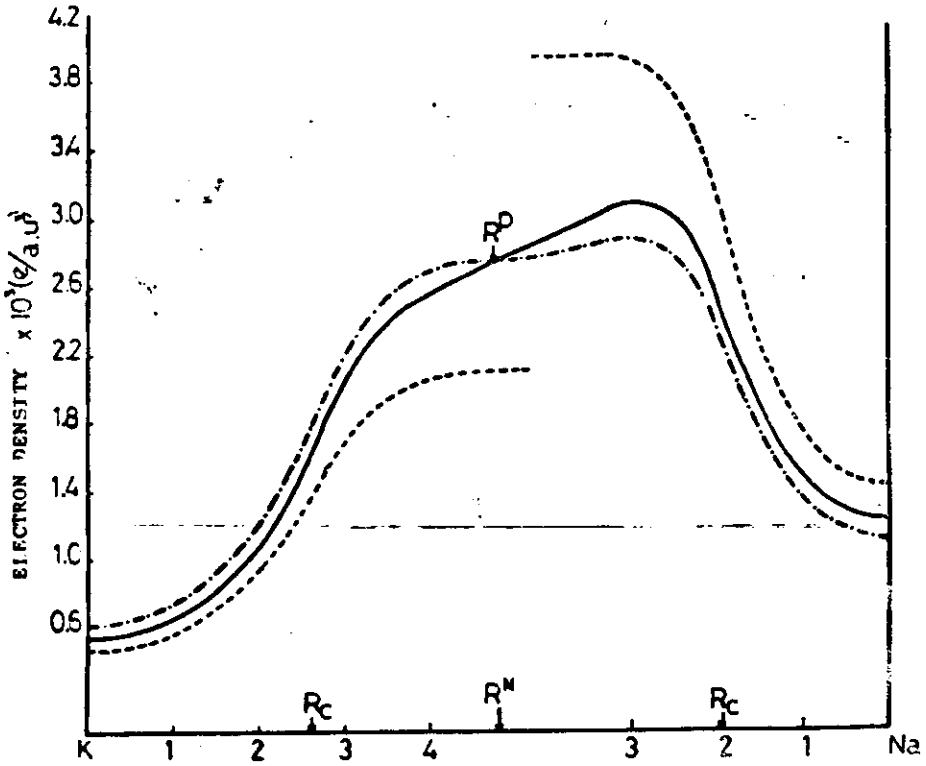


Figure 1 Iñiguez and Alonso

Miedema scheme for heat of mixing of alloys

$$\Delta H_{mix}(c) = c(1-c_s)\frac{2V_A^{2/3}}{\left(n_A^{-1/3}+n_B^{-1/3}\right)}\left[-P(\Delta\phi)^2+Q(\Delta n^{1/3})^2\right]$$

empirical numbers

$$c_s = \frac{cV_A^{2/3}}{cV_A^{2/3}+(1-c)V_B^{2/3}}$$

difference in metallic electronegativities

difference in electron densities at boundary of bulk cells

LIQUID STRUCTURE

$S(k)$, $g(r)$; $c(k)$, $c(r)$

$$g(r)-1 \equiv h(r) = \int \frac{d\underline{k}}{(2\pi)^3 n}\left[S(k)-1\right]e^{i\underline{k}\cdot\underline{r}}$$

$$c(k) = 1-\frac{1}{S(k)}\,, \qquad h(r) = c(r) + n\int d\underline{r}'\, c(|\underline{r}-\underline{r}'|)\,h(r')$$

---

random phase (RPA): $c(r) = -\phi(r)/k_BT$ (Debye-Hückel)

mean spherical (MSA): $\begin{cases} c(r) = -\phi(r)/k_BT & (r>\sigma) \\ g(r) = 0 & (r<\sigma) \end{cases}$

Percus-Yevick (PY): $c(r) = g(r)\left[1-e^{\phi(r)/k_BT}\right]$

hypernetted chain (HNC): $g(r) = \exp\left[-\frac{\phi(r)}{k_BT}+h(r)-c(r)\right]$

---

generalized mean spherical (GMSA)

modified hypernetted chain (MHNC)

optimized random phase (ORPA)

MHNC (Rosenfeld and Ashcroft 1979)

From diagrammatic analysis:

$$g(r) = \exp\left[-\frac{\phi(r)}{k_B T} + \underbrace{h(r) - c(r)}_{\hookrightarrow g(r)-1} - b(r)\right]$$

HNC sets $b(r) = 0$. "Bridge" graphs:

$b(r) =$  $+ \cdots$

$$= -\frac{1}{2} n^2 \iint d\underline{r}' d\underline{r}'' h(r') h(r'') h(\underline{r}' - \underline{r}'') h(\underline{r} - \underline{r}') h(\underline{r} - \underline{r}'') + \cdots$$

MHNC: estimate $b(r)$ from Percus-Yevick theory of neutral-hard-sphere liquid, with packing fraction η used to force thermodynamic consistency.

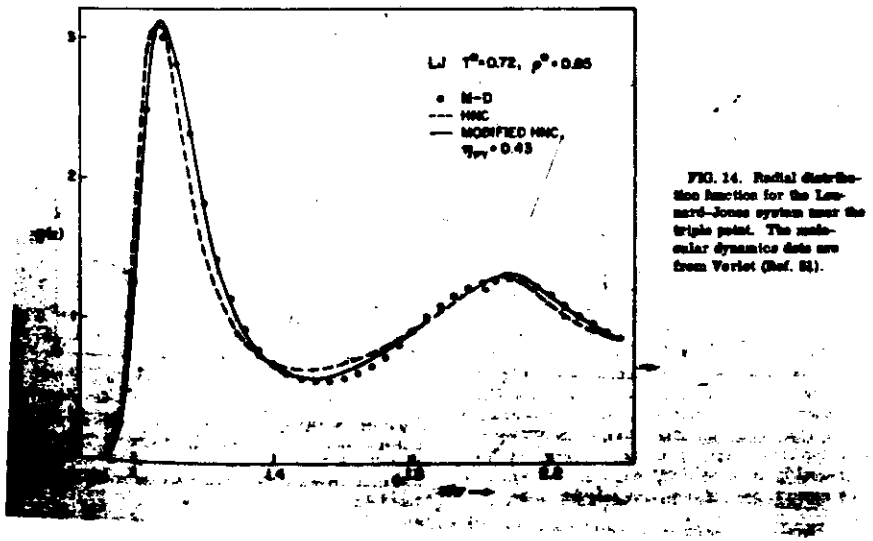


FIG. 14. Radial distribution function for the Lennard–Jones system near the triple point. The molecular dynamics data are from Verlet (Ref. 81).

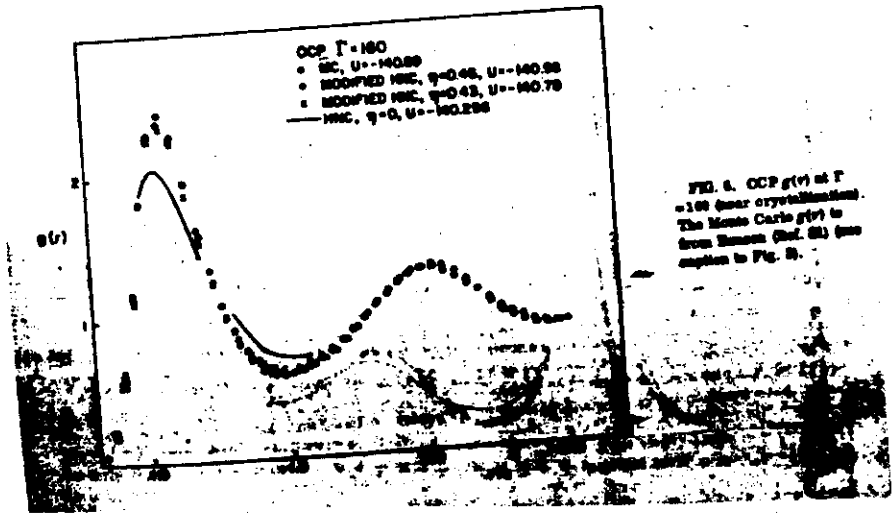


FIG. 6. OCP $g(r)$ at $\Gamma = 160$ (near crystallization). The Monte Carlo $g(r)$ is from Hansen (Ref. 62) [illegible] explain to Fig. 5.

Equimolar mixture of +e and +2e charges on neutralizing background – $\Gamma = 40$

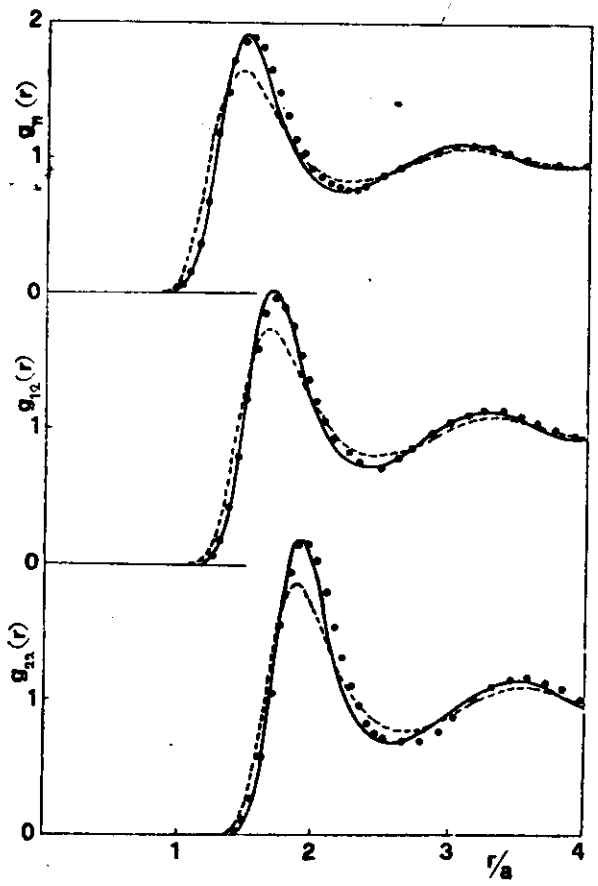


Fig.1

(Ballone et al 1984)

NaCl near freezing (Ballone et al 1984)

——— theory

····· simulation (Singer et al 1975)

oooo neutron diffraction (Biggin & Enderby 1982)

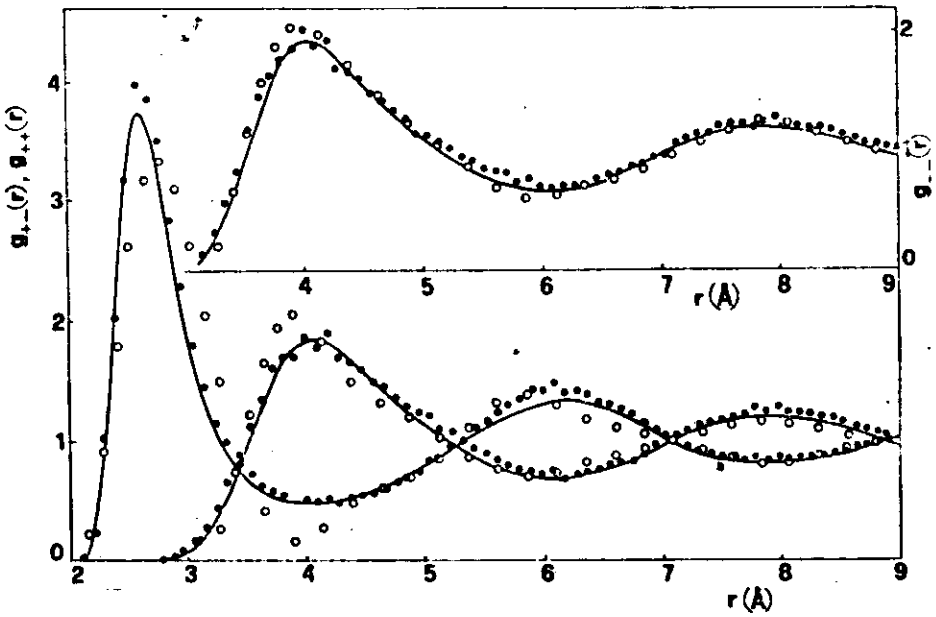


Fig.2

Other recent approaches to classical plasma structure (strong coupling)

- MHNC version by Ichimaru et al (1982):

  take $b(r) \propto b^{(w)}(r)$ with rescaling

- GMSA (Chatterjee et al 1981):

  construct $c(r)$ so that

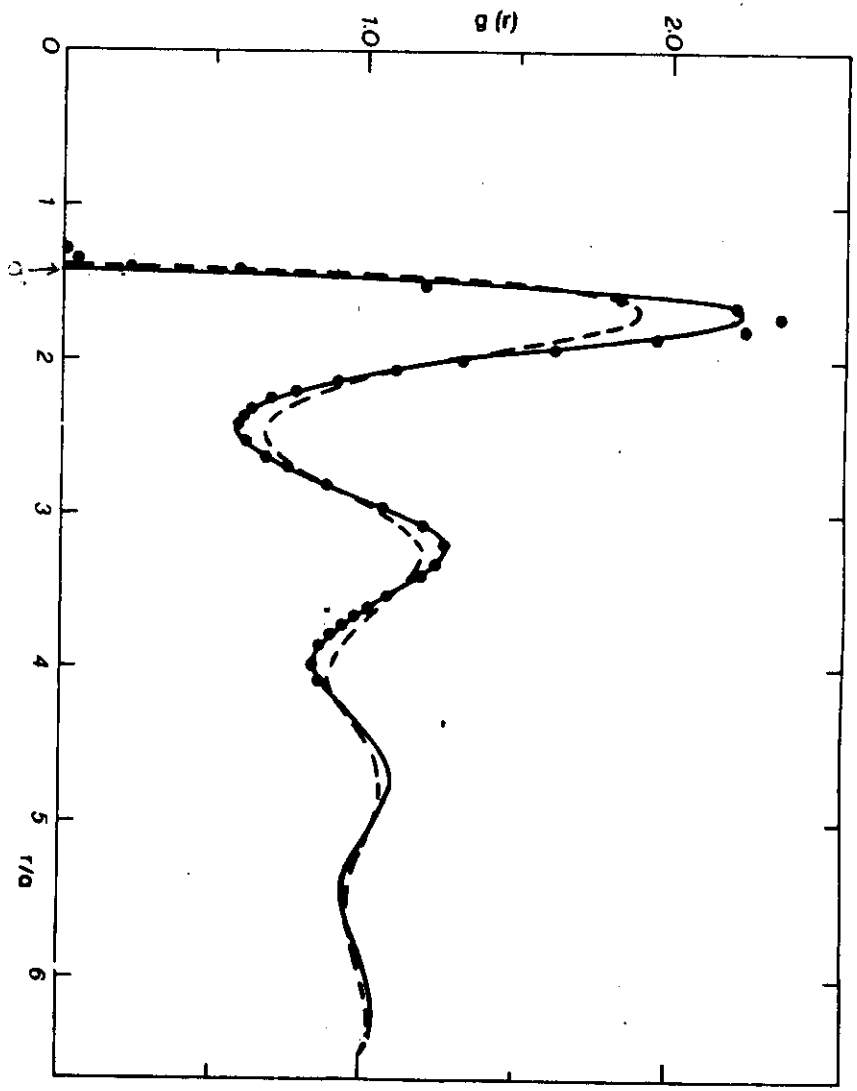
  (a) $g(r) = 0$ within excluded volume region ($r < \sigma$)

  (b) approach smoothly Debye-Hückel limit

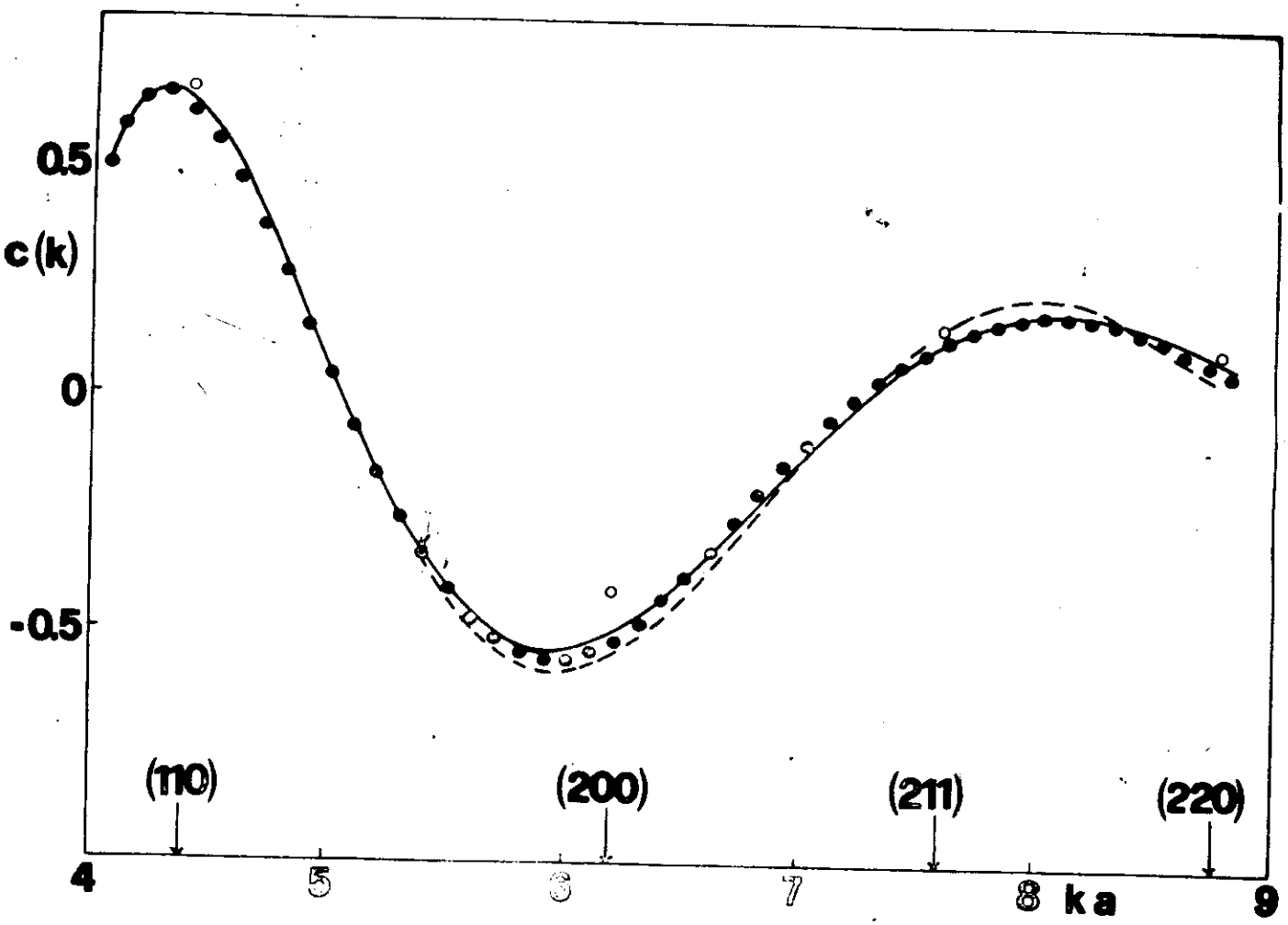
  $$c(r) \underset{r \to \infty}{\longrightarrow} -e^2/\epsilon k_B T$$

  (c) obtain thermodynamic consistency and equation of state from simulation data

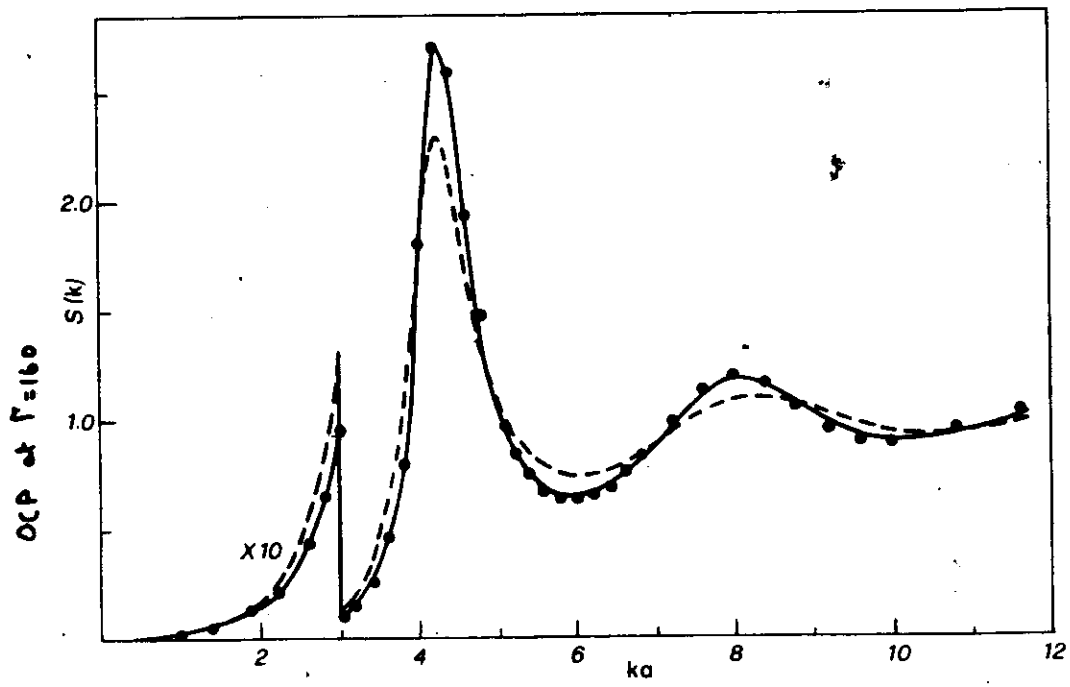
OCP at $\Gamma = 160$

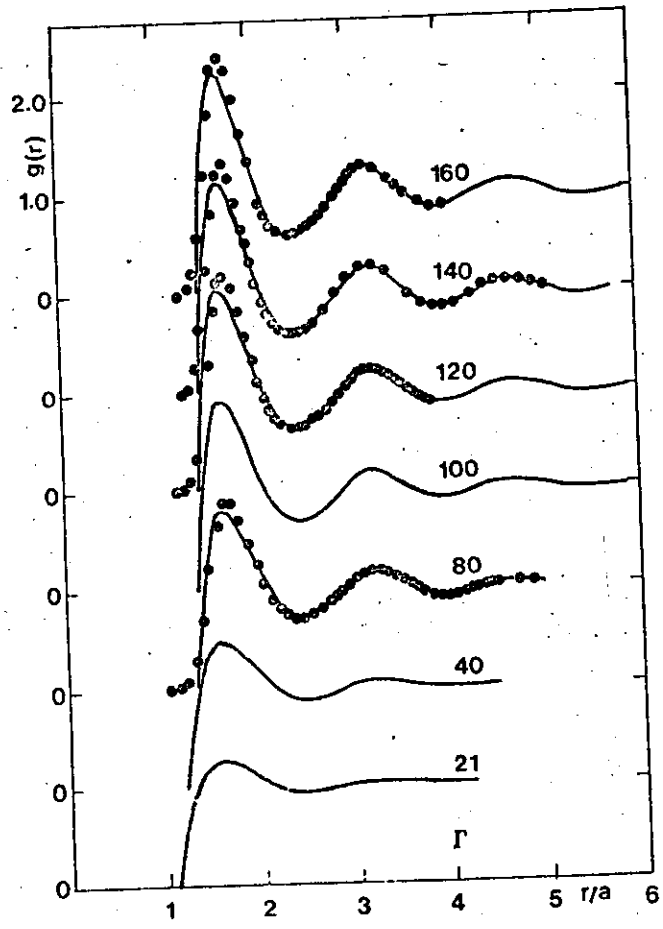


Γ=160

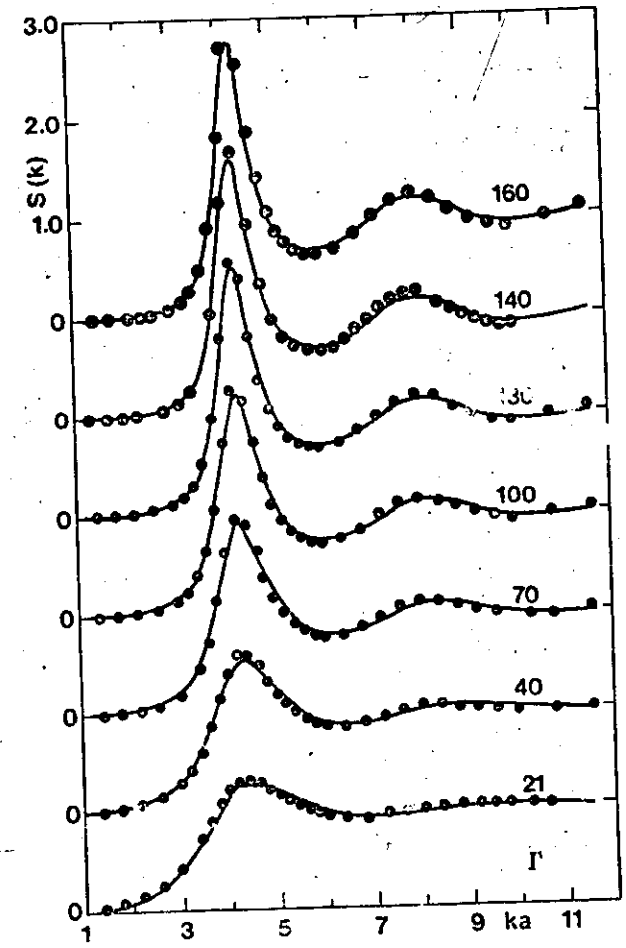

0.5
c(k)
0
-0.5
(110)
(200)
(211)
(220)
4
5
6
7
8
ka
9

(26)


OCP at T=150
S(k)
2.0
1.0
X10
2
4
6
8
10
12
ka



OCP : comparison between collective result MSA and computer simulation



$$I(k) = N\,|f(k)|^2\,S(k) \qquad k = \frac{4\pi}{\lambda}\sin\vartheta$$

ORPA for liquid alkali metals (Pastore & Tosi 1984)

Chandler, Weeks and Andersen (1971): perturbation theory on hard-sphere reference liquid. ORPA scheme for including attractive potential.

Classical plasma reference for liquid alkalis:

$$\Phi(r) = \frac{e^2}{r} + u(r) \qquad u(k) = -\frac{v^2(k)}{4\pi e^2/k^2}\left[1 - \frac{1}{\varepsilon(k)}\right]$$

RPA: $c(k) = c_{OCP}(k) - \dfrac{n\,u(k)}{k_B T}$

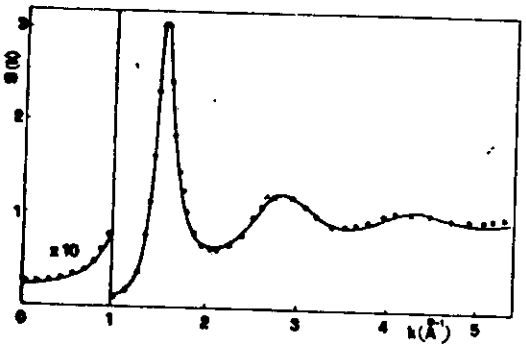
ORPA: replaces $u(r)$ by $\bar{u}(r)$ such that

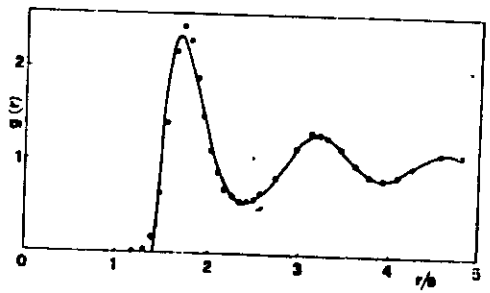
(a) $\bar{u}(r) = u(r)$ for $r > \sigma$

(b) $g(r) = 0$ for $r < \sigma$

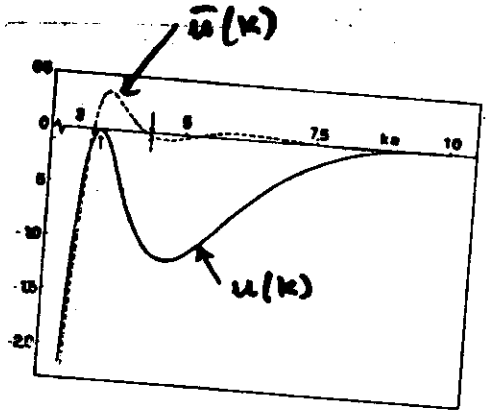
(b) is equivalent to variational condition on RPA free energy.

Rb (simul.)





SICS



Na

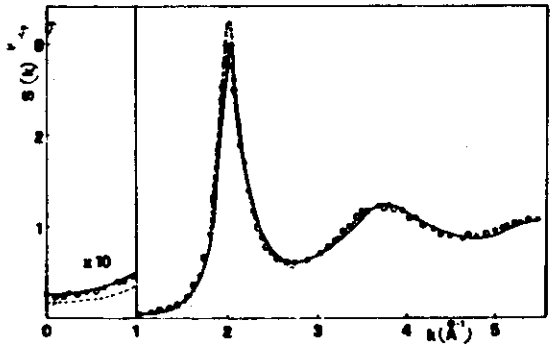
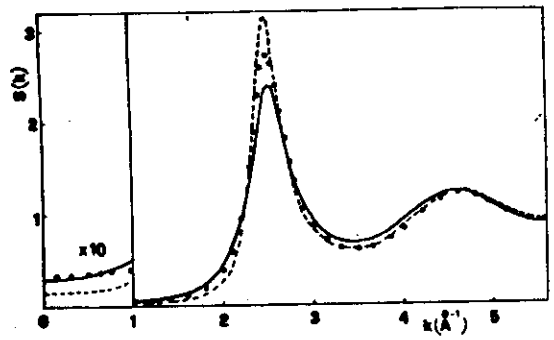
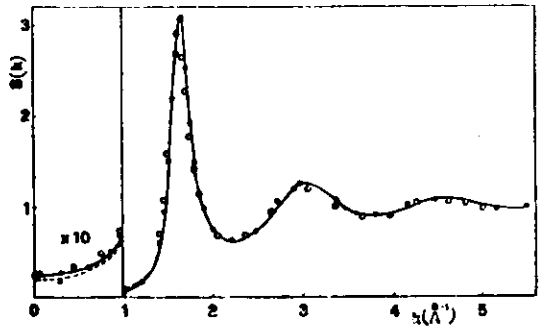


Fig. 1

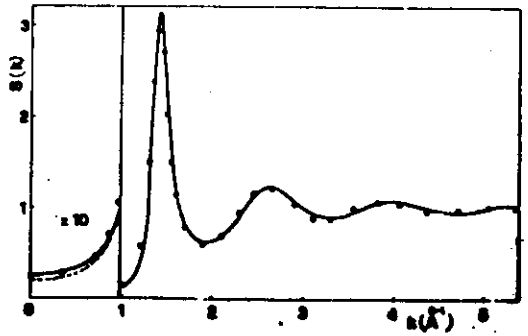
Li



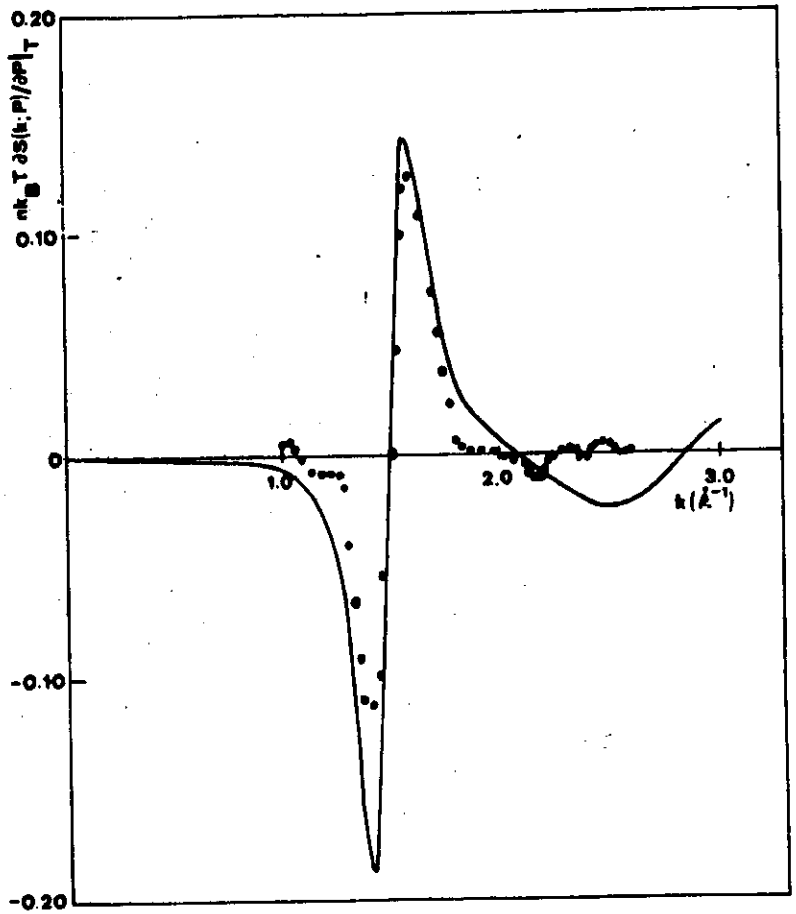
K



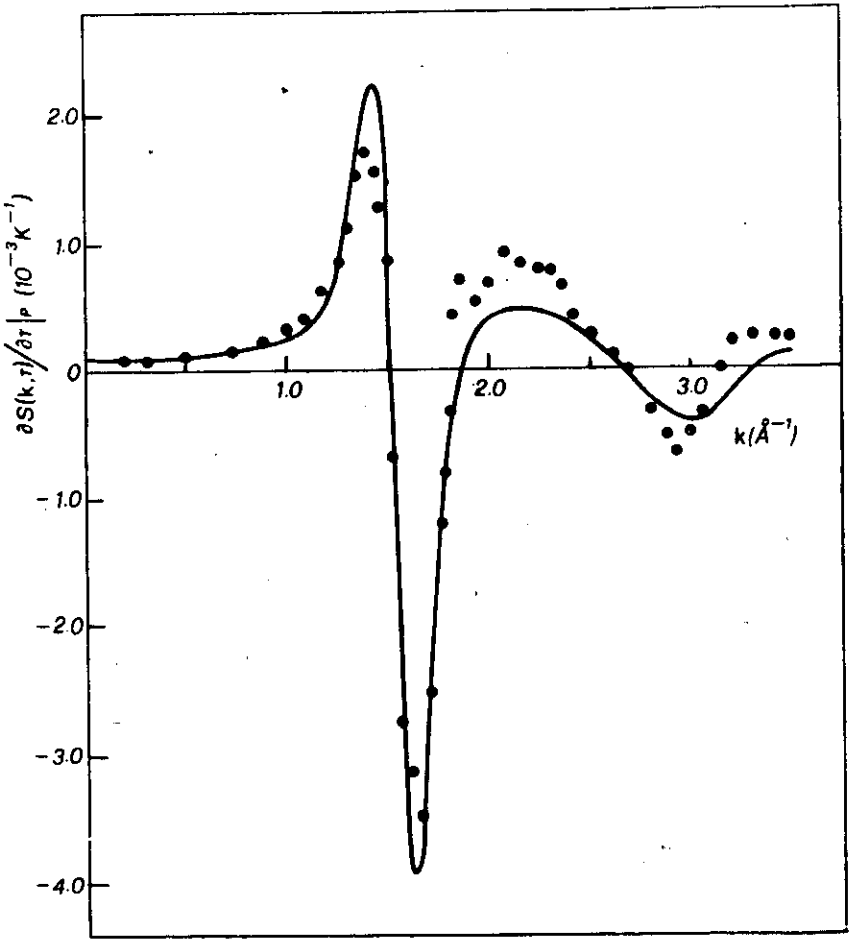
Cs

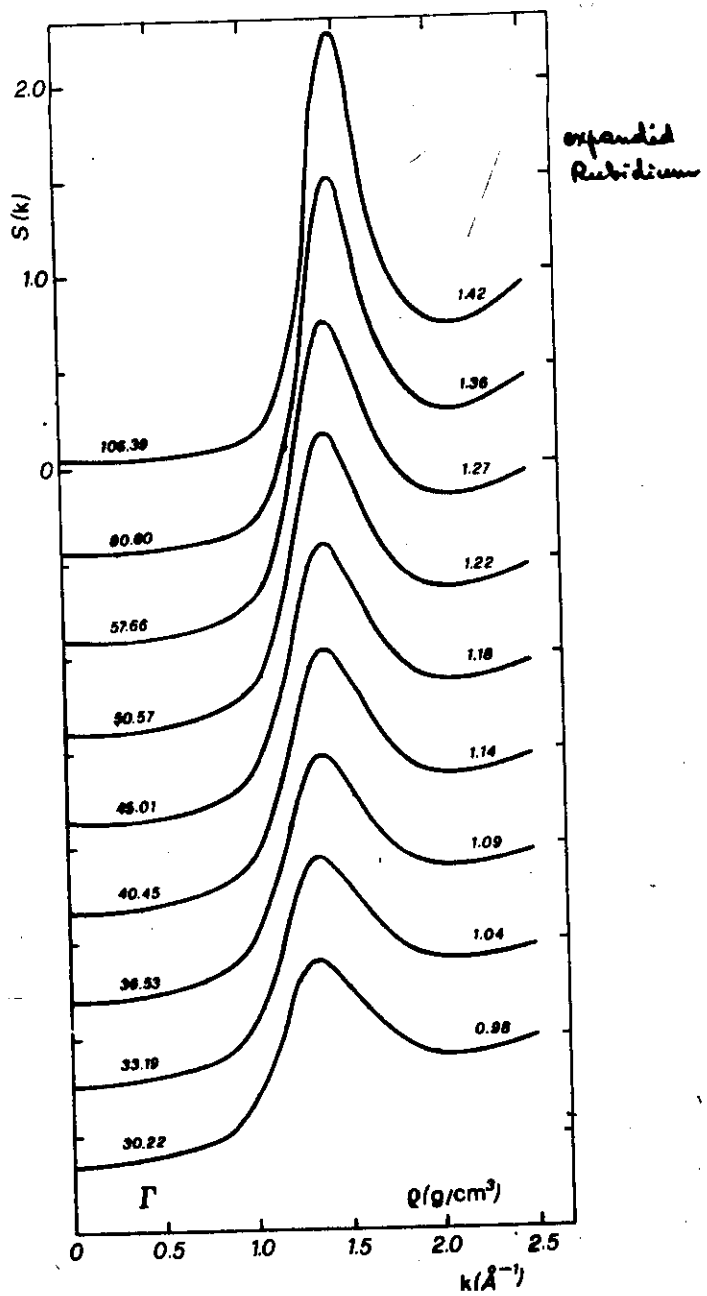


liquid Rb - theory (full curve) against neutron diffraction data



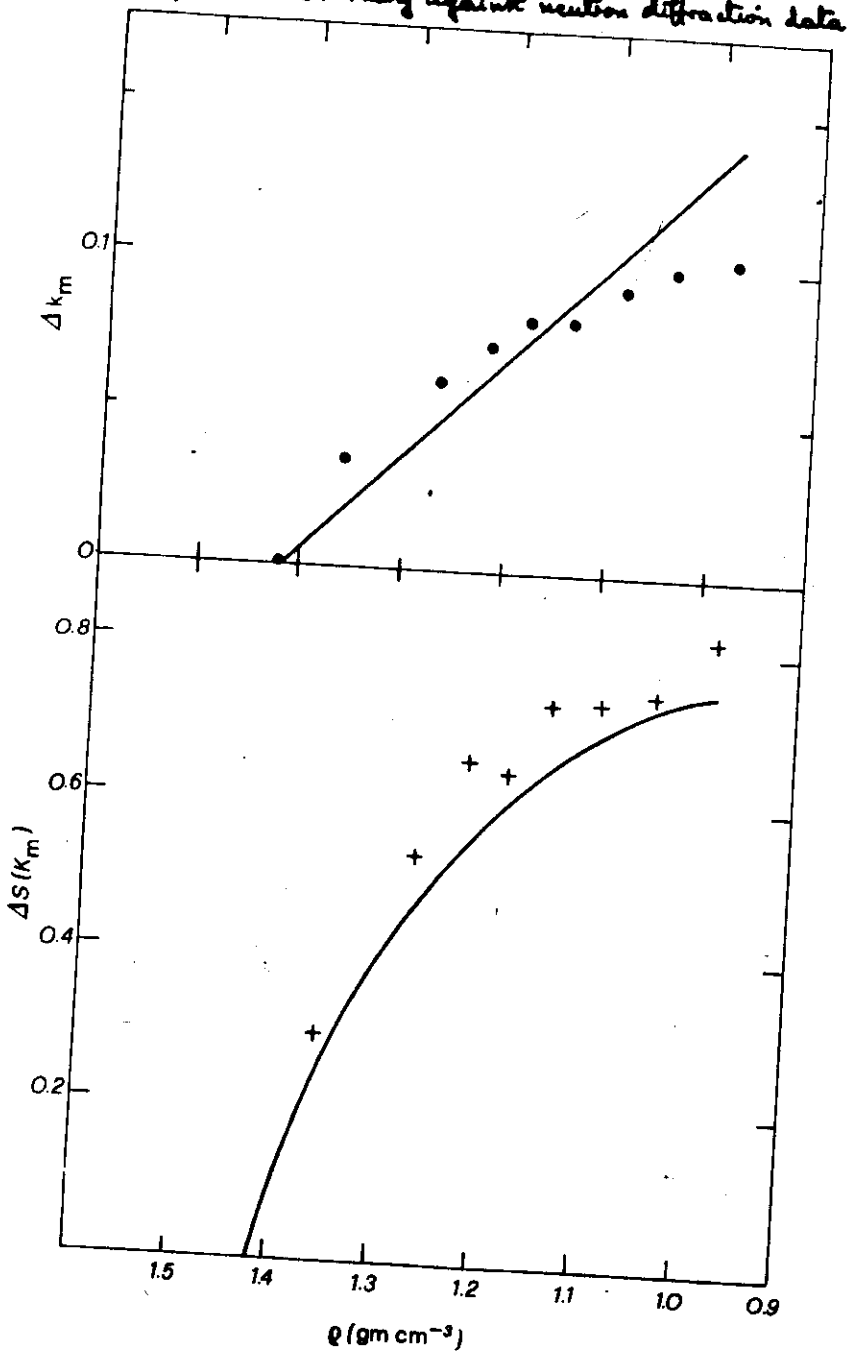
Liquid Na - theory against X-ray diffraction data

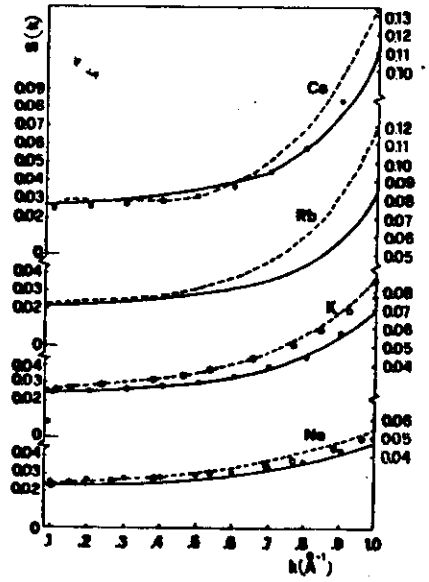




expanded Rb : theory against neutron diffraction data (37)

see also (6)





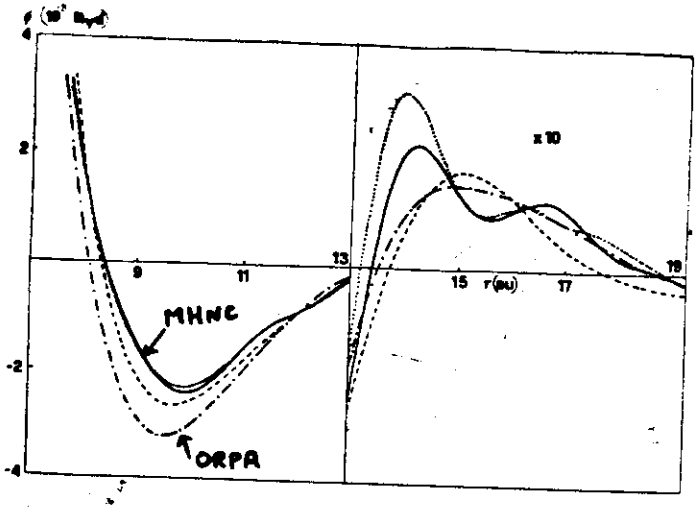


Fig.1

Rb

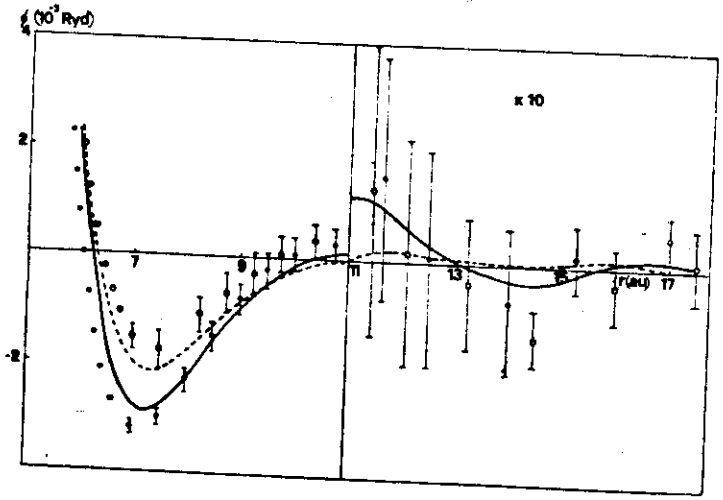


Fig.2

Na

Kumaravadivel (1984)

References to recent work on hydrogenic plasmas

Simulation in quasi-classical regime — J P Hansen and I R McDonald, Phys. Rev. letters 41, 1379 (1978)

Variational approach: L Lantto et al, in press

Liquid state theories: J. Chihara, in press
S Tanaka & S. Ichimaru, in press

Ground state theory and simulation:

A.H MacDonald & C.P. Burgess, Phys Rev. B26, 2849 (1982)
A.E. Carlsson & N.W. Ashcroft, Phys. Rev B29, 479 (1984)
D.M. Ceperley & B.J. Alder, Physica 108B, 875 (1981).