

## Structure study of simple fluids

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**Abstract.** The structure function of simple monatomic liquids like neon and argon is studied in an approximation scheme where intermediate function  $Q(r)$  is extended beyond hardcore diameter rather than the direct correlation function  $C(r)$ . The calculated values show good agreement with experimental values.

**Keywords.** Ornstein-Zernike equation; structure function; intermediate function; direct correlation function; total correlation function.

### 1. Introduction

There have been substantial new developments in the characterisation of structure and thermodynamics of a classical monatomic liquid at equilibrium (Barker and Henderson 1976). The exponential approximations (EXPA) of Andersen and Chandler (1972) and the optimised random phase approximation (ORPA) (Andersen and Chandler 1971) are both refined theories. The EXPA and ORPA give highly accurate results for the structure function,  $S(k)$  of liquid for all  $k \geq 5 \text{ \AA}^{-1}$  (Stell and Weis 1980). However striking differences emerge among the hard sphere (HS), ORPA, EXPA and renormalised hypernetted chain approximation (RHNC) results, and between each of them and the Monte-Carlo (MC) results, for smaller  $k$ . The most unexpected and disquieting features of the small  $k$  results is that EXPA takes on negative values at liquid state densities and temperatures (Stell and Weis 1980).

In a recent paper, Deo and Naik (1983, hereafter denoted as paper I) have developed a novel approximation formalism where correlation functions of hard-sphere system are evaluated in an elegant way. The purpose of the present paper is to calculate the structure function of simple dense fluids like argon and neon, utilising the above technique.

The calculated values of  $S(k)$  agree well with the neutron diffraction data of deGraff and Mozer (1971) for liquid neon and x-ray diffraction data of liquid argon by Aisenstein and Gingrich (1942) for all  $k$ . The merit of the work lies in the fact that it gives good correspondence with low  $k$  region.

In §2 we briefly review the formalism of paper I and deduce the expression for  $S(k)$ . The calculated result of  $S(k)$  is compared with those of HS and the experiment both in tabular and graphical form in §3.

### 2. Formalism

The Ornstein-Zernike (oz) (1926) relation for a classical homogeneous fluid with

central forces can be written as

$$h(r) = C(r) + \rho \int d\mathbf{r}' C(r') h(\mathbf{r} - \mathbf{r}'), \tag{1}$$

where  $r$  and  $r'$  are the magnitudes of vectors  $\mathbf{r}$  and  $\mathbf{r}'$ ,  $\rho$  is the particle number density,  $C(r)$  is the direct correlation function and  $h(r)$  is the total correlation function. The three-dimensional Fourier transform of oz equation is

$$\tilde{h}(k) = \tilde{C}(k) + \rho \tilde{C}(k) \tilde{h}(k), \tag{2}$$

where  $\tilde{h}(k)$  and  $\tilde{C}(k)$  are the three-dimensional Fourier transform of  $h(r)$  and  $C(r)$  respectively. From (2) it can be shown that

$$1 + \rho \tilde{h}(k) = 1/[1 - \rho \tilde{C}(k)]. \tag{3}$$

Let us introduce a new function  $\tilde{A}(k)$ , defined by

$$\tilde{A}(k) = 1 - \rho \tilde{C}(k), \tag{4}$$

such that  $1 + \rho \tilde{h}(k) = 1/\tilde{A}(k)$ .  $\tag{5}$

For a disordered fluid  $\tilde{h}(k)$  is finite and from (5) it follows that  $\tilde{A}(k)$  can have no zeros in the real  $k$  axis. When this is so  $\tilde{A}(k)$  can be factorised as (Baxter 1968),

$$\tilde{A}(k) = \tilde{Q}(k) \tilde{Q}(-k), \tag{6}$$

where the function  $\tilde{Q}(k)$  is regular, has zeros in the lower half plane and can be written in the form

$$\tilde{Q}(k) = 1 - 2\pi\rho \int_0^R dr \exp(ikr) Q(r), \tag{7}$$

$Q(r)$  being a real function.  $S(k)$  is given by the relation

$$S(k) = 1 + \rho \tilde{h}(k) = 1/\tilde{A}(k) = 1/[\tilde{Q}(k) \tilde{Q}(-k)]. \tag{8}$$

$S(k)$  calculated by (7) and (8) gives the structure function values of a dense fluid assumed to be an assembly of hard spheres in the Percus-Yevic (PY) approximation. It is found to yield values of  $S(k)$  in serious disagreement with experiment in the low  $k$  region.

In paper I an approximation scheme is suggested where  $Q(r)$  and  $C(r)$  exist beyond the hard core till say,  $R + \sigma$ . The Baxter (1968) equation becomes

$$Q'(r) = -r h(r) + 2\pi\rho \int_0^{R+\sigma} dt (r-t) h(|r-t|) Q(t), \tag{9}$$

for  $r < R$ .

Equation (9) reduces to

$$Q'(r) = Ar + B + 2\pi\rho \int_R^{R+\sigma} dt (r-t) g(|r-t|) Q(t), \tag{10}$$

where  $A = 1 - 2\pi\rho \int_0^R Q(t) dt - 2\pi\rho \int_R^{R+\sigma} Q(t) dt,$   $\tag{11}$

and  $B = 2\pi\rho \int_0^R t Q(t) dt + 2\pi\rho \int_R^{R+\sigma} t Q(t) dt.$   $\tag{12}$

The last term in (10) does not vanish in the region for small  $r$ ,  $0 < r < \sigma$ . So  $Q'(r)$  for  $r < R$  is not necessarily linear in  $r$ . However, expanding  $g(r)$  near  $r \simeq R$  to the lowest order in  $\sigma$  the last term in (10) becomes

$$2\pi\rho \int_R^{R+\sigma} dt(r-t)[g(R) + (R-t+r)g'(R-t+r) + \dots]Q(t).$$

Hence (10) will reduce to

$$Q'(r) = Ar + B + 2\pi\rho g(R) \int_R^{R+\sigma} Q(t) dt(r-t) \tag{13}$$

which is linear.

Introducing a change of variable

$$Z = 2(r - R)/\sigma - 1, \tag{14}$$

and using the conditions

$$Q_\infty(z)_{z=-1} = Q(R) = 0, \tag{15a}$$

$$Q_\infty(z)_{z=1} = Q(R + \sigma) = 0, \tag{15b}$$

$$-2\pi\rho \frac{\sigma}{2} \int_{-1}^1 Q_\infty(z) dz = D, \tag{15c}$$

and 
$$-2\pi\rho \frac{\sigma}{2} \int_{-1}^1 Q_\infty(z)z dz = 0, \tag{15d}$$

we find that for  $r > R$ ,

$$Q_\infty(z) = a_1 + a_2z + a_3z^2 + a_4z^3 + a_5z^4, \tag{16}$$

where  $a_1 = (15K - Q'\sigma)/8; \quad a_2 = 0 \tag{17a, b}$

$$a_3 = Q'\sigma/2 - 2a_1; \quad a_4 = 0 \tag{17c, d}$$

$$a_5 = -(a_1 + a_3); \quad K = -D/2\pi\rho\sigma \tag{17e, f}$$

and  $Q'\sigma$  is the derivative of  $Q_\infty(z)$  at  $z = -1$ .

In the approximation scheme the Fourier transform of  $\tilde{Q}(k)$  is assumed to be of the form

$$\tilde{Q}(k) = \tilde{Q}_{hc}(k) + \tilde{Q}_\infty(k), \tag{18}$$

where  $\tilde{Q}_{hc}(k)$  is given by (7) and

$$Q_\infty(k) = -2\pi\rho \int_R^{R+\sigma} \exp(ikr)Q(r)dr. \tag{19}$$

Transforming the integral in (19) to the  $z$  variable one gets

$$\tilde{Q}_\infty(k) = -2\pi\rho\sigma \exp[ik(R + \sigma/2)] \int_0^1 \exp(ik\sigma z/2)Q(z) dz, \tag{20}$$

which is more amenable to direct computation. Designating the real and imaginary part of  $\tilde{Q}_h(k)$  as  $U$  and  $V$  and that of  $\tilde{Q}_\infty(k)$  as  $U_\infty$  and  $V_\infty$  the structure function is given by

$$S(k) = 1/[(U + U_\infty)^2 + (V + V_\infty)^2]. \tag{21}$$

Equation (21) is used for the numerical evaluation of the structure function.

### 3. Numerical results

The monatomic inert element liquids are most suitable for a comparison of experimental result with theory. That is the reason why both neon and argon are chosen. Experimental data (deGraff and Mozer 1971) for neon are available at three different densities of  $1.0624$ ,  $1.1190$  and  $1.1630 \times 10^3 \text{ kg/m}^3$ . At  $1.0624 \times 10^3 \text{ kg/m}^3$  density, the  $S(k)$  calculated in the present paper is compared with the corresponding HS values using the PY approximation together with the experimental result in table 1. The results are also plotted in figure 1 for comparison.  $R$  is taken as  $2.75 \text{ \AA}$  (Temperley and Trevena 1978),  $\sigma$  is taken as  $0.03 \text{ \AA}$  for the best fit.  $k$  is varied up to  $12.5 \text{ \AA}^{-1}$ . Similarly for density  $1.1190$  and  $1.1630 \times 10^3 \text{ kg/m}^3$ , the calculated values are shown in tables 2 and 3 and the plots in figures 2 and 3 respectively. In the low  $k$  region the HS result is in disagreement with the experiment in all the densities. But the computed results in our formalism show good correspondence in the low as well as high  $k$  region.

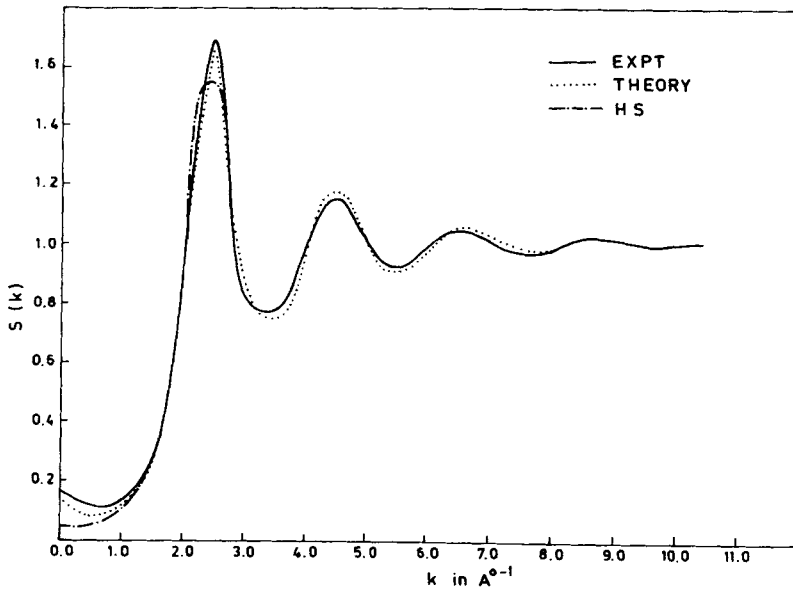
Aisenstein and Gingrich (1942) have obtained x-ray diffraction pattern of argon for 26 different conditions of pressure and temperature ranging from  $0.8$  atmosphere and  $84.35^\circ\text{K}$  to  $51.1$  atmosphere and  $168^\circ\text{K}$  with variation of density from  $1.401 \times 10^3 \text{ kg/m}^3$  to  $0.038 \times 10^3 \text{ kg/m}^3$ . We have chosen only two representative types of

**Table 1.** Calculated values of  $S(k)$  for liquid neon compared with HS and experimental result (density:  $1.0624 \times 10^3 \text{ kg/m}^3$ ).

$k\text{\AA}^{-1}$	Experimental	Theory	HS
0.0	0.160	0.154	0.064
0.5	0.115	0.075	0.074
1.0	0.125	0.117	0.118
1.5	0.244	0.269	0.277
2.0	0.932	0.982	0.996
2.5	1.692	1.688	1.574
3.0	0.821	0.893	0.902
3.5	0.760	0.744	0.781
4.0	1.016	0.934	0.952
4.5	1.161	1.214	1.148
5.0	1.006	1.085	1.055
5.5	0.919	0.887	0.925
6.0	0.981	0.896	0.936
6.5	1.045	1.058	1.032
7.0	1.020	1.120	1.059
7.5	0.976	0.982	0.992
8.0	0.981	0.904	0.954
8.5	1.007	0.974	0.988
9.0	1.017	1.009	1.033
9.5	0.997	1.051	1.019
10.0	0.988	0.941	0.979
10.5	0.994	0.993	0.976
11.0	1.005	1.030	1.008
11.5	0.997	1.081	1.002
12.0	0.998	0.995	1.000
12.5	0.998	0.929	0.981

**Table 2.** Same as table 1 (density:  $1.119 \times 10^3 \text{ kg/m}^3$ ).

$kA^{-1}$	Experimental	Theory	HS
0.0	0.117	0.106	0.054
0.5	0.078	0.064	0.063
1.0	0.095	0.100	0.100
1.5	0.203	0.232	0.237
2.0	0.834	0.901	0.916
2.5	1.774	1.785	1.677
3.0	0.797	0.888	0.895
3.5	0.738	0.727	0.758
4.0	0.992	0.923	0.940
4.5	1.164	1.202	1.166
5.0	1.000	1.061	1.064
5.5	0.902	0.885	0.917
6.0	0.969	0.923	0.927
6.5	1.054	1.056	1.035
7.0	1.025	1.060	1.067
7.5	0.974	0.984	0.991
8.0	0.979	0.966	0.948
8.5	1.016	0.984	0.986
9.0	1.020	1.055	1.037
9.5	0.992	1.049	1.022
10.0	0.989	0.954	0.977
10.5	1.000	0.986	0.973
11.0	1.007	1.028	1.008
11.5	1.003	1.075	1.025
12.0	0.998	0.997	1.000
12.5	1.001	0.984	0.979



**Figure 1.** Theoretically calculated values (dotted line) and HS values (chained line) of  $S(k)$  for liquid neon compared with experimental result (solid line) for density  $1.0624 \times 10^3 \text{ kg/m}^3$ .

**Table 3.** Same as table 1 (density: 1.1630  $\times 10^3$  kg/m<sup>3</sup>).

$k\text{\AA}^{-1}$	Experimental	Theory	HS
0.0	0.086	0.084	0.048
0.5	0.057	0.056	0.056
1.0	0.077	0.088	0.089
1.5	0.170	0.206	0.210
2.0	0.765	0.831	0.845
2.5	1.864	1.879	1.771
3.0	0.787	0.885	0.890
3.5	0.718	0.711	0.738
4.0	0.992	0.953	0.928
4.5	1.172	1.203	1.182
5.0	1.003	1.057	1.072
5.5	0.893	0.882	0.910
6.0	0.961	0.928	0.920
6.5	1.051	1.056	1.037
7.0	1.027	1.023	1.074
7.5	0.967	0.984	0.991
8.0	0.960	0.905	0.944
8.5	1.009	0.983	0.984
9.0	1.016	1.084	1.041
9.5	0.987	1.050	1.024
10.0	0.988	0.965	0.975
10.5	0.995	0.987	0.971
11.0	1.007	1.026	1.009
11.5	0.999	1.004	1.027
12.0	1.000	0.997	1.001
12.5	1.000	0.986	0.977

**Table 4.** Calculated values of  $S(k)$  for liquid argon compared with HS and experimental result (density: 1.401  $\times 10^3$  kg/m<sup>3</sup>).

$k\text{\AA}^{-1}$	Experimental	Theory	HS
0.000	0.049	0.049	0.028
0.628	0.100	0.040	0.040
1.001	0.142	0.072	0.072
1.256	0.200	0.132	0.135
1.638	0.545	0.555	0.571
1.884	2.125	2.136	1.957
1.998	2.638	2.601	2.384
2.261	2.055	1.996	1.257
2.513	0.812	0.746	0.760
2.890	0.738	0.726	0.655
3.141	0.960	0.751	0.781
3.518	1.250	1.202	1.167
3.605	1.545	1.302	1.240
3.769	1.428	1.369	1.281
4.126	1.181	1.045	1.032
4.775	0.833	0.820	0.863
5.403	1.285	1.152	1.099
6.031	1.0	0.998	0.999
6.660	1.0	0.950	0.993

Table 5. Same as table 4 ( $0.87 \times 10^3 \text{ kg/m}^3$ ).

$kA^{-1}$	Experimental	Theory	HS
0.000	0.5	0.474	0.118
0.628	0.3	0.169	0.169
1.005	0.321	0.294	0.302
1.256	0.5	0.502	0.522
1.633	1.09	1.221	1.207
1.872	1.38	1.511	1.413
1.884	1.497	1.508	1.409
2.261	1.142	1.062	1.042
2.513	0.943	0.864	0.889
2.890	0.88	0.826	0.870
3.141	0.884	0.921	0.948
3.518	0.92	1.025	1.077
3.769	1.09	1.154	1.086
4.146	1.1	1.108	1.003
4.775	1.0	0.997	0.954
5.403	1.142	1.091	1.036
6.031	0.932	0.930	0.997
6.660	1.0	0.985	0.978

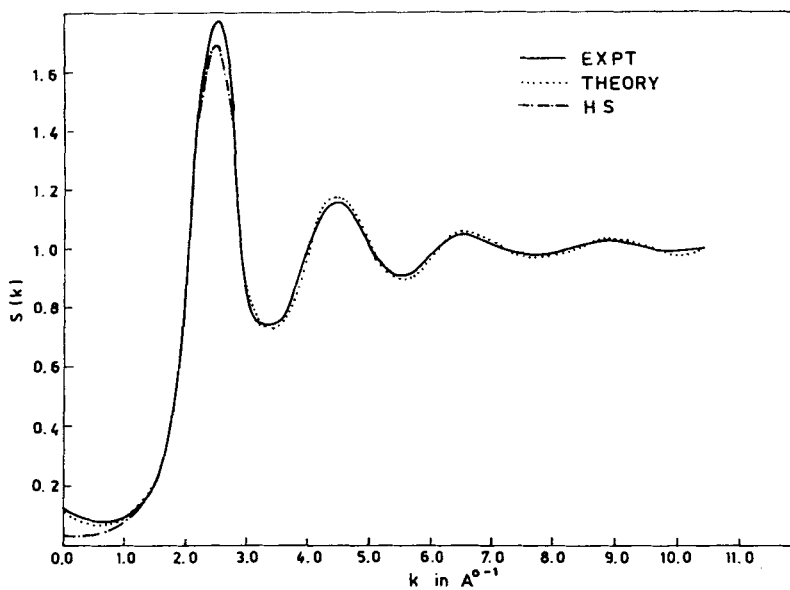


Figure 2. Same as figure 1 for density  $1.119 \times 10^3 \text{ kg/m}^3$ .

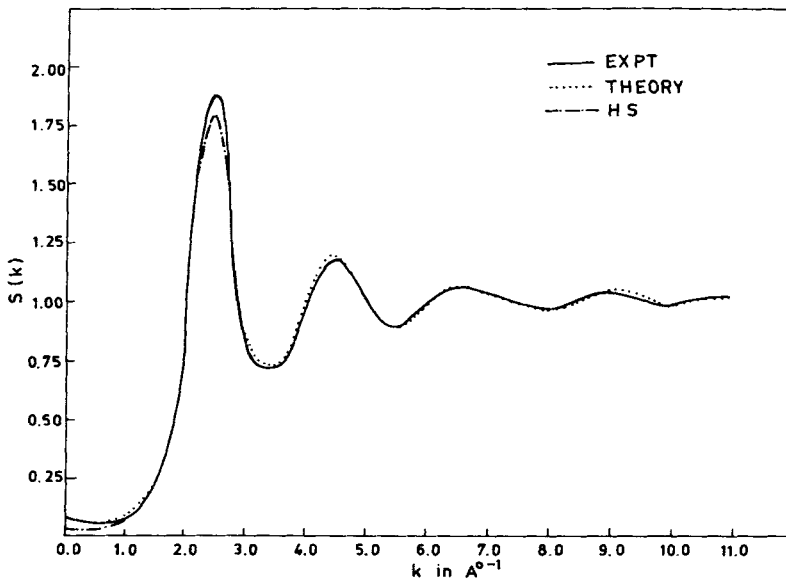


Figure 3. Same as figure 1 for density  $1.1630 \times 10^3 \text{ kg/m}^3$ .

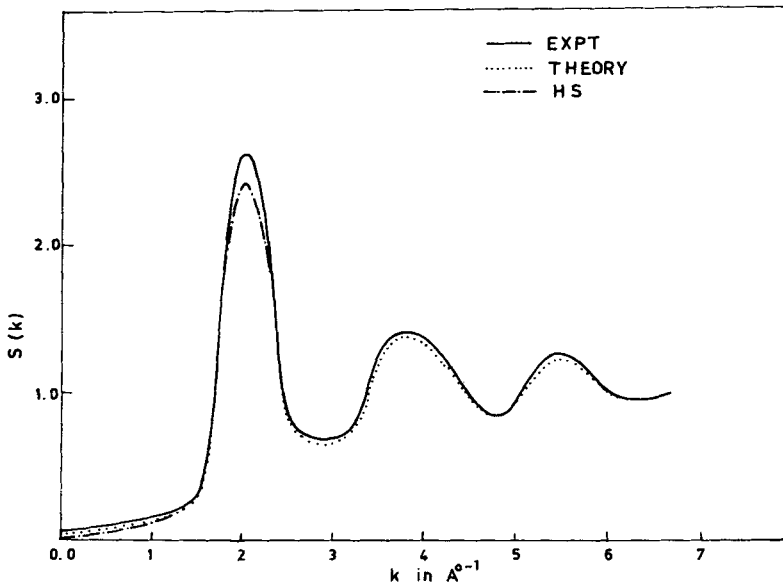


Figure 4. Theoretically calculated values (dotted line) and HS value (chained line) of  $S(k)$  for liquid argon compared with experimental result (solid line) for density  $1.401 \times 10^3 \text{ kg/m}^3$ .



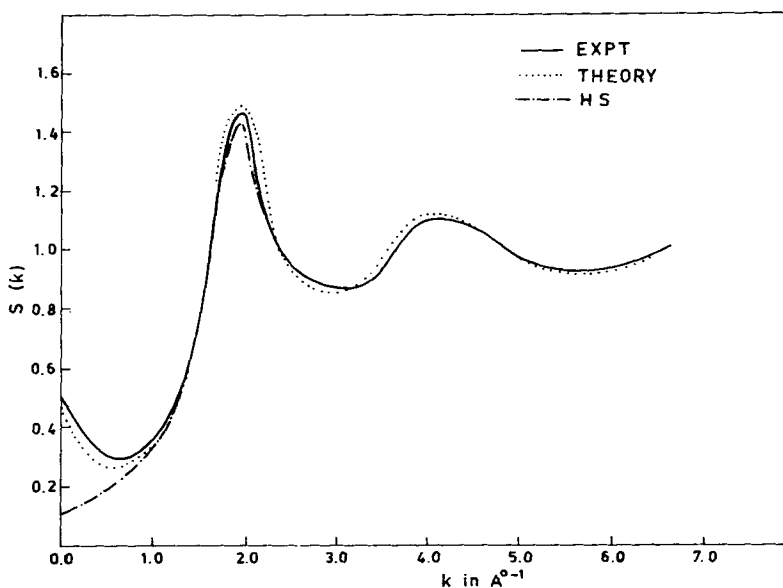


Figure 5. Same as figure 4 at density  $0.87 \times 10^3 \text{ kg/m}^3$ .

density of  $1.401 \times 10^3 \text{ kg/m}^3$  at  $84.4^\circ\text{K}$  and  $0.87 \times 10^3 \text{ kg/m}^3$  at  $144.1^\circ\text{K}$ . The intensity pattern given in electron units against  $\sin \theta/\lambda$  is converted to the corresponding  $S(k) \sim k$  values. For density  $1.401 \times 10^3 \text{ kg/m}^3$ , the  $S(k)$  calculated in our formalism is compared with the corresponding HS values using PY approximation together with the experimental result (Aisenstein and Gingrich 1942) in table 4. The results are plotted in figure 4 for comparison.  $R$  is taken as  $3.405 \text{ \AA}$  (Temperley and Trevena 1978) and  $\sigma$  is taken as  $0.02 \text{ \AA}$  for the best fit. Similarly for density  $0.870 \times 10^3 \text{ kg/m}^3$ , the calculated values are shown in table 5 and the plots in figure 5. For liquid argon also the HS results show discrepancy in the low  $k$  region. But our results show good agreement with experiment.

#### 4. Conclusion

In the PY approximation  $C(r)$  is strictly zero beyond the hard core diameter  $R$ . The structure function of liquid alkali metals (Ashcroft and Lekner 1966) like sodium, potassium and rubidium gives good correspondence with experiment when calculated for the HS system using PY approximation. This is so because ion-ion interaction in them is the dominant feature in the interatomic potential  $u(r)$ . But in  $S(k)$  of liquids like argon and neon the PY approximation shows disagreement in the low  $k$  region. It is suggested by Egelstaff (1967) that the detailed behaviour of  $S(k)$  is controlled by the tail of  $u(r)$  at large  $r$ . Addition of any attractive part to the HS potential makes the Baxter's formalism extremely complicated. This has been attempted by Smith (1978), Chaturbedi *et al* (1981a, b), Blum and Hoye (1978) and Deo *et al* (1982). In the present work, this fact is well taken into account by suitably extending  $Q(r)$  beyond hard core. Making use of this

approximation formalism we have got good correspondence of  $S(k)$  with experiment both in the low and high  $k$  region.

The advantage of this method lies in the fact that it gives  $C(r)$  for  $r > R$  directly from  $Q(r)$ . Therefore one clearly by-passes the difficulty of inverting the  $S(k)$  data. Once  $C(r)$  is known it also enables one to calculate the interatomic pair potential. This has been attempted in a separate paper.

The boundary condition for  $Q_\infty(r)$  given by (15c) has been so chosen as to give the desired  $\tilde{Q}(0)$  value. By (8),  $S(0)$  and  $\tilde{Q}(0)$  are related. So this  $\tilde{Q}(0)$  value gives the exact  $S(0)$  value.  $S(0)$  is again related to isothermal compressibility  $\chi_T$  (Egelstaff 1967) by

$$S(0) = \rho k_B T \chi_T, \quad (22)$$

where  $k_B$  is the Boltzmann constant. Thus  $S(0)$  gives the exact isothermal compressibility.

There has been a lot of interest in the study of classical one-component plasma. Chaturbedi *et al* (1981a, b) and Singh (1983) have used the mean spherical approximation to study its structure and correlation function of interest. Our formalism can also be used to calculate the same more easily and accurately.

Further, the structure study of polyatomic liquid has aroused interest recently. We feel that this new technique can be applied to solve this problem, and work along these lines is being pursued.

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