

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

Structural Parameters of Inert Liquids: Part I. Liquid Helium, Neon and Xenon

S. N. Bagchi^a; J. P. Supple^b

^a Physics Department, Loyola Campus, Concordia University, Montreal, Canada ^b Computel Systems Ltd., Ottawa, Canada

To cite this Article Bagchi, S. N. and Supple, J. P. (1979) 'Structural Parameters of Inert Liquids: Part I. Liquid Helium, Neon and Xenon', *Physics and Chemistry of Liquids*, 8: 4, 223 – 233

To link to this Article: DOI: 10.1080/00319107908084754

URL: <http://dx.doi.org/10.1080/00319107908084754>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Structural Parameters of Inert Liquids

Part I. Liquid Helium, Neon and Xenon

S. N. BAGCHI

Physics Department, Loyola Campus, Concordia University, Montreal, Canada

and

J. P. SUPPLE

Computel Systems Ltd., Ottawa, Canada

(Received June 19, 1978)

Radial distribution functions of liquid helium, neon and xenon at various temperatures and pressures published by different authors have been analysed by the method given before (Bagchi 1972). The relevant significant structural parameters of these liquids are given in the tables. The figures show how the theoretical curves fit the experimental curves and also show the distribution of individual neighbours.

I INTRODUCTION

The importance of pair distribution function in the theory of liquids is well known. Unfortunately, a theoretical calculation of the pair distribution function for a given interacting potential is beset with many difficulties and no satisfactory method has yet been devised. Consequently, the determination of the pair distribution function from experimental data is of considerable interest. The usual method is to determine this from scattering experiments, in particular from X-ray and neutron diffraction experiments. The radial distribution function (RDF), $4\pi r^2 g(r)$, is obtained from the scattered intensity data in a straightforward way. But in order to get the relevant parameters of the scattered substance one must analyse this RDF correctly. It has been proved previously (Bagchi 1970, 1972) that the conventional method of analysis of RDF by putting Gaussian curves at the humps of this function is mathematically and physically incorrect.

The correct method of analysis of RDF, given in Bagchi (1970, 1972), has been utilised to analyse the RDF of various simple liquids and several important structural parameters have been obtained from such analyses. It is believed that this method offers more reliable and more detailed structural parameters of the liquid state than is possible to obtain by any other method of RDF analysis. Moreover, the data seem to be sufficiently accurate for the calculation of many other relevant properties of liquids in equilibrium conditions. Since the inert liquids are of special importance for theoretical investigations on the theory of liquid state, in this paper and in the next, the data on RDF functions of inert liquids found in the literature have been analyzed by the method discussed in detail by Bagchi (1972). Some of the data on Argon which had been presented there have been analysed more accurately. Part I gives the data on Helium, Neon and Xenon and Part II gives liquid Argon at various temperatures and pressures.

II METHODOLOGY

For convenience, we give here a brief outline of the method used to analyse the RDF. For details see Bagchi (1972).

The RDF, $4\pi r^2 g(r)$, was taken from the published literature. One was obtained from neutron diffraction, the rest from scattered X-ray intensity.

It is to be noted that the function $g(r)$ is the convolution square of the density function ρ . Consequently, in order to get the distribution functions of neighbours we have to deconvolute $g(r)$. There is an analytic solution of $g(r)$ (see Hosemann and Bagchi 1952), but we shall not use this complicated and involved solution. Instead, as illustrated and discussed in detail by Bagchi (1970, 1972), we shall fit the given $4\pi r^2 g(r)$ curve by choosing properly, by least squares methods, the probability distribution of the first neighbour $H_1(r)$. As shown before, for simple liquids this will give the probability distribution of the n th neighbour as

$$H_n(r) = \sum_p H_p(r)$$

$$H_p(r) = \frac{1}{4\pi^{3/2} m^{1/2} \alpha r_p} \frac{1}{r} \left\{ \exp - \frac{(r - r_p)^2}{m\alpha^2} - \exp - \frac{(r + r_p)^2}{m\alpha^2} \right\}$$

The summation is to be taken over all the atoms belonging to the given n th neighbour. It is determined by the coordination number C_n . The location of the centroid of the p th atom is r_p . $\alpha^2/2 = \Delta^2 r$ denotes the mean square fluctuation in any direction of the nearest distance vector (n.d.) from r_p , its most probable value. m denotes the number of convolutions by which the

pth atom is reached from the origin with the help of uncorrelated fundamental vectors of the nearest neighbours.

We start from the values corresponding to the known crystal structures at 0°K and fit the curve by varying α , r , and C simultaneously. The numbering of neighbours and the values of m for each neighbour has been determined from the known structure of the liquids in their solid states.

This method obviously presupposes that the liquid is statistically homogeneous. In the previous paper, it has been shown that in spite of surprisingly good fits by this method, the liquid states—even in simple liquids like Argon—consist of clusters. But in most cases these clusters do not affect the analysis of $g(r)$ functions and consequently of the pair distribution function $n_2(r)$. But in a few cases the slight discrepancy found previously has been corrected by introducing an additional distribution function representing the distance statistics of the first intercluster distance. Higher order interactions were not considered because of computational difficulties.

III RESULTS

The figures show the experimental values as crosses (+ + +) and the calculated values as solid (—) curves, and also the distributions of various neighbours. In many cases, in order to avoid clumsiness, only the neighbour statistics of the lowest curve have been given. The superposition of these neighbour statistics gives the resulting theoretical RDF. As emphasized previously, (Bagchi 1970, 1972), one must attempt to get a good overall fit, in particular those at higher distances. The values of Σ^2 given in Tables II and IV represent the sum of least squares for about 75 equidistant points and is a measure of the overall closeness of the fit. The divergences at the tail end of the figures are due to taking into consideration only a few neighbour statistics. We did not think it worthwhile to spend more computer time for a better fit. We believe the values given in the tables are quite adequate to describe the significant structural parameters of the liquid state.

The structural parameters α , $\Delta^2 r$, $\Delta^2 a$, $|P_c|$, L_c , $|P_L|$, and L have been given in Tables I and III.

$\Delta^2 a = \Delta^2 r - \Delta^2 s$, where $\Delta^2 a$, $\Delta^2 s$ are the mean-square displacements in any direction due to the distortion of the lattice positions themselves, and due to thermal vibrations corresponding to $\Delta^2 r$, the mean-square fluctuation of the first neighbour distance. $\Delta^2 s$ is calculated from Debye's theory of specific heat.

$|P_c| \approx \varepsilon^2 (r_1 / \Delta r)^2$, ($\varepsilon \approx 0.43$), = the number of nearest neighbours corresponding to the correlation length L_c of $n_2(r)$.

$|P_L| \approx (r_1 / \Delta a)$ = the interaction zone of the lattice.

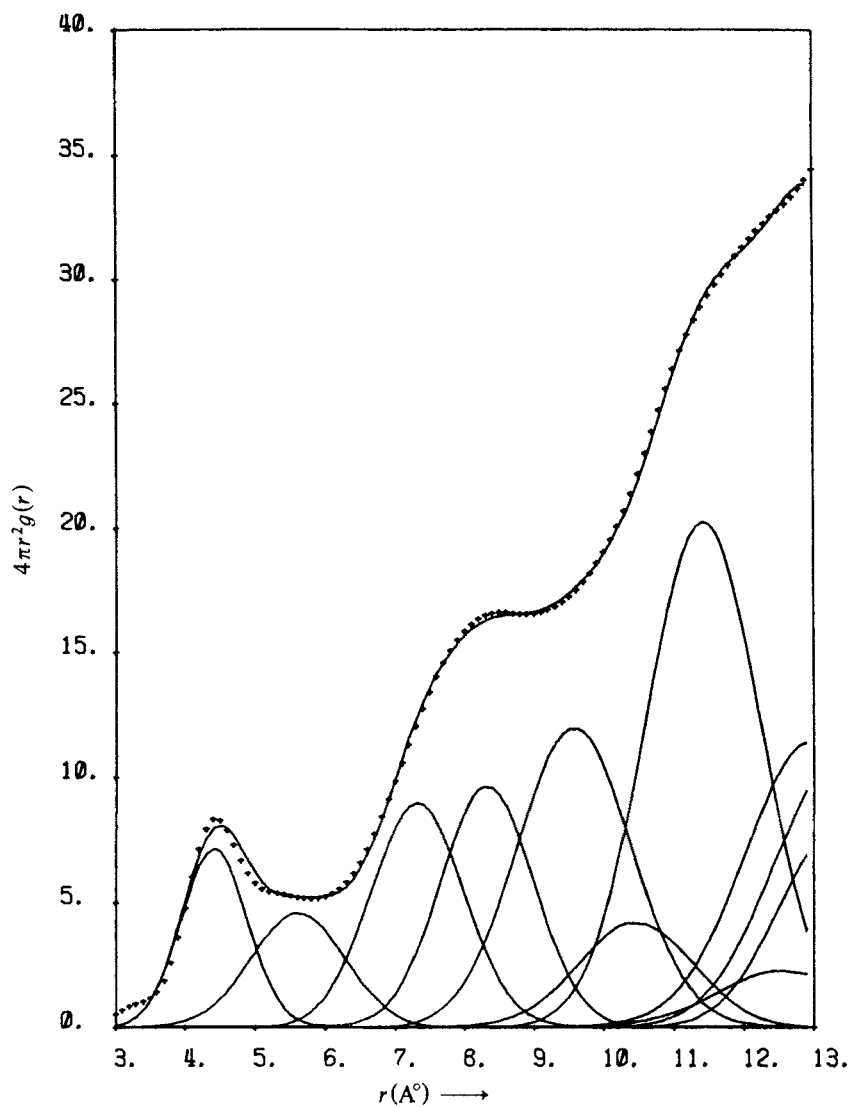


FIGURE 1 Xenon 161.5 K. Experimental (+ + +) and calculated (—) RDF by varying all parameters simultaneously. Also shown are neighbours (—).

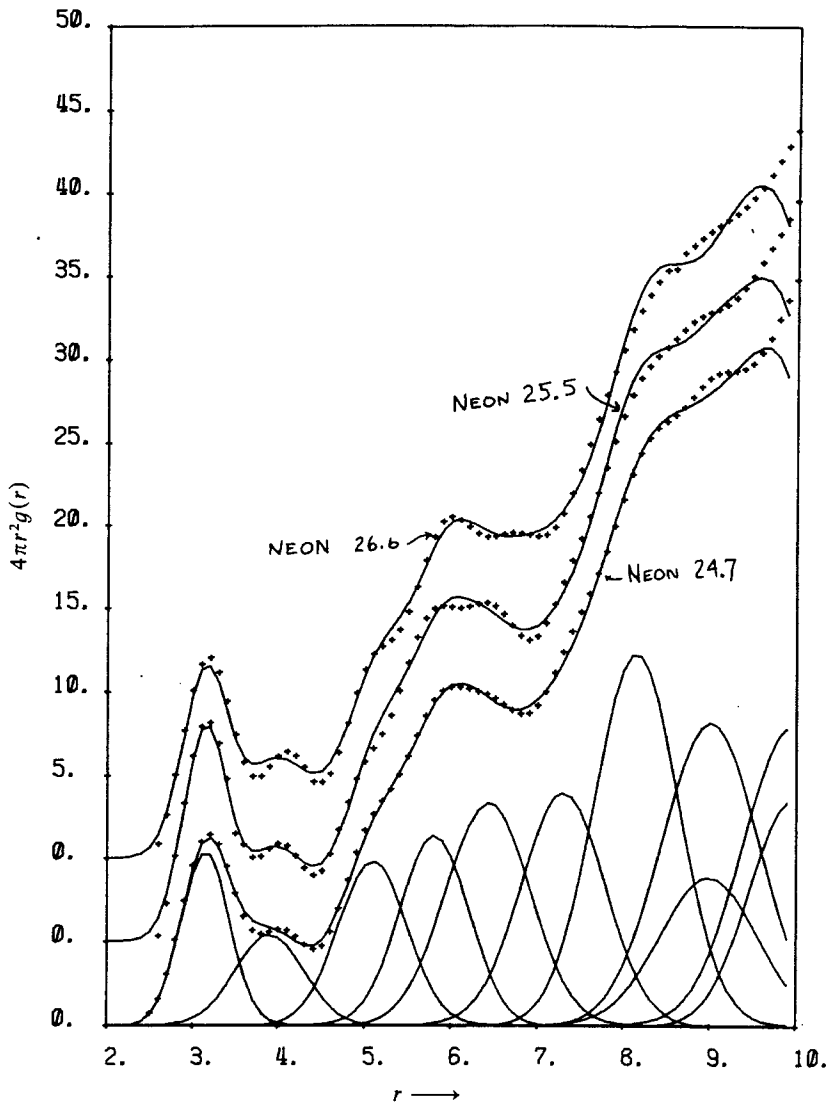


FIGURE 2 Neon 24.7, 25.5 and 26.6 K. Experimental (+ + +) and calculated (—) RDF by varying all parameters simultaneously. Also shown are neighbours for Neon 24.7 K. For clarity vertical scales are successively shifted by 5 units.

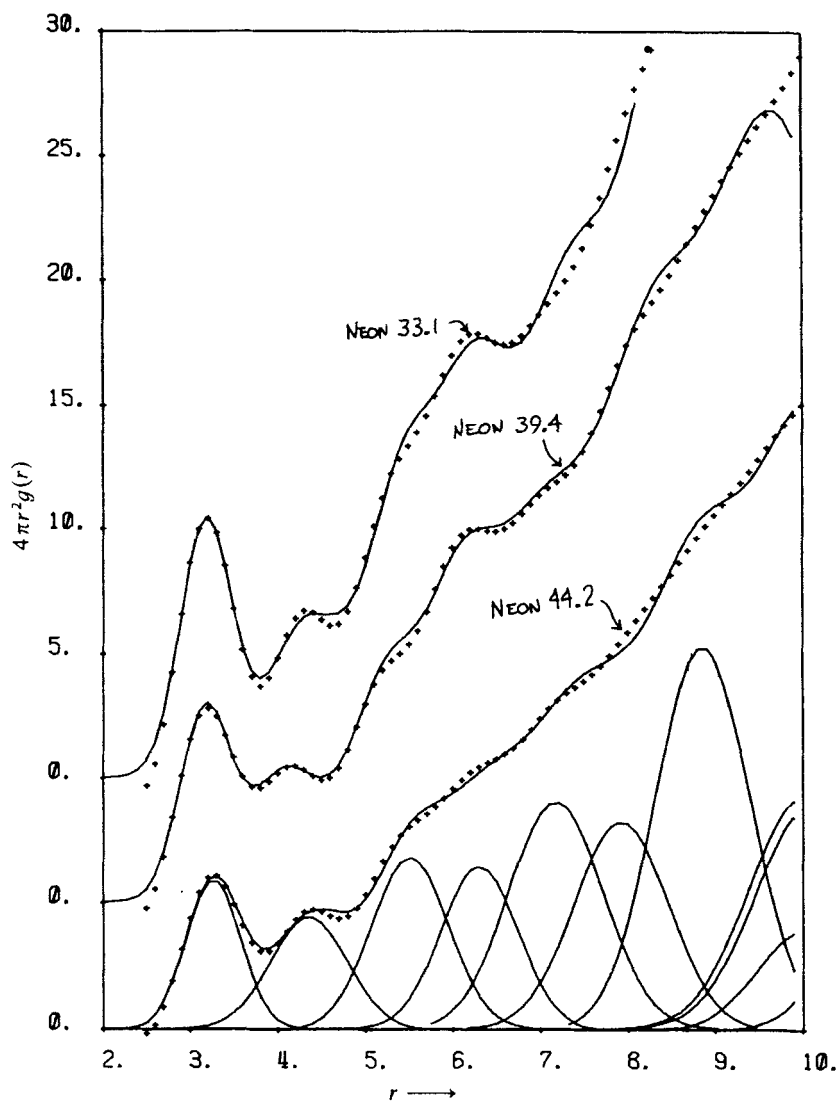


FIGURE 3 Neon 33.1, 39.4 and 44.2 K. Experimental (+ + +) and calculated (—) RDF by varying all parameters simultaneously. Also shown are neighbours for Neon 44.2 K. Vertical scales are successively shifted by 5 units.

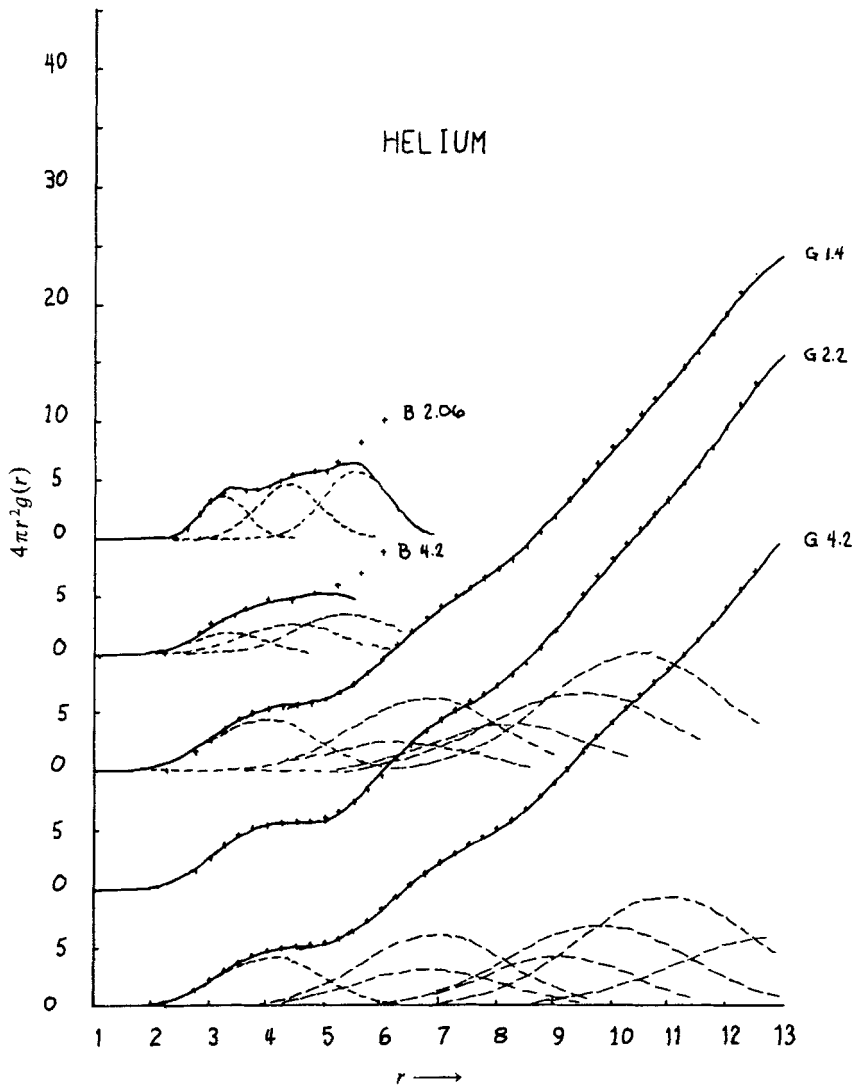


FIGURE 4 Helium. From top to bottom: Beaumont and Reekie 2.06 and 4.2 K, Gordon 1.4, 2.2 and 4.2 K. Experimental (+ + +) and calculated (—) RDF by varying all parameters. Neighbours (---) are shown for all but Gordon 2.2 K. Vertical scales are shifted by 5 units.

TABLE I
Structural parameters of xenon and neon

	Xenon	Neon	Neon	Neon	Neon	Neon	Neon
T (°K)	161.5	24.7	25.5	26.6	33.1	39.4	44.2
θ (°K)	55	64	64	64	64	64	64
α	0.6673	0.3984	0.3671	0.3834	0.4200	0.4100	0.4400
r_1	4.352	3.117	3.127	3.126	3.163	3.149	3.224
$\Delta^2 r$	0.2227	0.0794	0.0674	0.0735	0.0882	0.0841	0.0968
$\Delta r/r_1$ %	10.84	9.038	8.301	8.671	9.388	9.206	9.651
$ p_c $	21	31	36	33	28	29	27
L_c (Å)	19.94	17.35	18.76	17.96	16.74	16.96	16.75
$\Delta^2 s$	0.0589	0.0505	0.0518	0.0536	0.0637	0.0738	0.0817
$\Delta^2 a$	0.1637	0.0289	0.0156	0.0198	0.0245	0.0103	0.0151
$\Delta a/r_1$ %	9.298	5.453	3.992	4.506	4.952	3.220	3.811
$ P_L $	116	336	628	492	408	965	689
L (Å)	93.74	114.3	156.7	138.7	127.8	195.7	169.2

TABLE II
Neighbour statistics for xenon and neon

	Xenon	Neon 24.7	Neon 25.5	Neon 26.6	Neon 33.1	Neon 39.4	Neon 44.2
Σ^2	5.6502	7.9656	18.256	20.356	31.187	5.1257	4.7238
α	0.66731	0.39841	0.36713	0.38335	0.42000	0.41000	0.44000
m	r/C	r/C	r/C	r/C	r/C	r/C	r/C
1	4.352	3.117	3.127	3.126	3.163	3.149	3.224
	8.455	7.296	8.191	7.509	7.687	5.540	4.604
2	5.544	3.866	3.954	3.968	4.289	4.067	4.320
	7.654	5.379	5.089	5.605	6.476	5.396	4.881
2	7.244	5.053	5.086	5.102	5.406	5.200	5.461
	14.99	9.779	9.379	9.982	11.98	8.694	7.494
2	8.275	5.784	5.769	5.878	6.238	6.060	6.279
	16.12	11.35	11.02	13.17	14.16	10.85	7.133
3	9.490	6.385	6.397	6.573	7.180	6.907	7.128
	24.44	16.28	16.97	16.14	17.20	15.18	12.20
3	10.40	7.277	7.272	7.385	7.642	7.656	7.899
	8.614	17.06	15.42	15.53	9.916	10.17	11.13
3	11.35	8.116	8.088	8.213	8.544	8.298	8.821
	41.51	27.16	27.85	29.73	35.48	19.25	20.66
4	12.51	8.970	8.981	9.131	9.659	9.175	9.978
	5.339	12.52	12.14	12.25	8.048	8.799	14.39
3	13.23	8.971	8.982	9.136	9.659	10.23	9.978
	15.94	25.63	25.28	24.33	12.18	7.055	5.303
4	12.89	9.928	9.907	9.969	9.802	9.231	10.05
	26.98	16.50	13.53	11.51	24.73	19.39	13.82

TABLE III
Structural parameters of helium

	Gordon helium	Gordon helium	Gordon helium
T (°K)	1.4	2.2	4.2
θ (°K)	40	40	40
α	1.300	1.193	1.281
r_1	3.694	3.715	3.845
$\Delta^2 r$	0.8454	0.7116	0.8202
$\Delta r/r_1$	24.89	22.71	23.56
$ P_c $	4	5	5
L_c	7.388	8.306	8.597
$\Delta^2 s$	0.0381	0.0600	0.1139
$\Delta^2 a$	0.8073	0.6517	0.7063
$\Delta a/r_1$	24.32	21.73	21.86
$ P_L $	17	21	21
L	30.46	34.05	35.24

TABLE IV
Neighbour statistics of helium

	Gordon 1.4	Gordon 2.2	Gordon 4.2	Beaumont 2.06	Beaumont 4.20
Σ^2	2.527	0.8219	0.3843	0.2067	0.3040
α	1.300	1.193	1.281	0.5477	0.8789
m	r/C	r/C	r/C	r/C	r/C
1	3.694 9.849	3.715 9.768	3.845 9.312	3.194 3.573	3.247 2.953
2	6.058 7.668	6.099 8.461	6.647 9.985	4.273 6.311	4.183 5.668
2	6.497 19.86	6.508 19.30	6.679 19.40	5.470 7.914	5.237 7.536
2	8.058 12.75	7.942 12.24	8.949 13.60		
3	9.132 26.05	9.208 25.75	9.524 26.75		
3	9.795 4.157	9.786 7.149	9.808 3.216		
3	10.17 39.35	10.13 38.86	10.76 36.33		
4	11.27 6.348	11.31 4.789	11.36 3.996		
3	12.22 18.89	12.16 17.11	12.51 13.46		
4	12.20 31.15	12.10 29.38	12.75 26.62		

$L \approx 2|P_L|$ = linear dimension of the lattice. For theoretical derivations of these relations, see Refs. 1 and 2.

The values of the distance, r_n , of the successive neighbours, the coordination number, C_n , of these neighbours as well as the values of α used in the calculation are given in the tables.

Experimental data on liquid Xenon, in equilibrium with its vapour at the temperature of 161.5°K (near the triple point) and with $b = 0.035$ were taken from the dissertation of Harris, kindly supplied by Professor Hendrew of the University of Arkansas, Fayetteville, Arkansas U.S.A. For the experimental methodology see Harris and Clayton (1967).

Experimental data on Neon were taken from Schmidt and Tompson (1968). The temperatures, pressures and densities for the six samples are given below.

T (°K)	P (Atm)	(gm/cc)
24.7	0.485	1.25
25.5	0.595	1.23
26.6	0.88	1.22
33.1	4.6	1.09
39.4	13.2	0.92
44.2	26.9	0.67

The experimental data on Helium by Gordon *et al.* were also taken from Schmidt and Tompson. The relevant temperature, pressure and density are:

T (°K)	P (Atm)	(gm/cc)
1.4	0.00284	0.1445
2.2	0.0533	0.146
4.2	0.986	0.1252

The data were compared with those obtained by Beaumont and Reekie (1955). Their data are comparatively meagre and do not extend as far. The samples were investigated at two temperatures 1.27 K and 4.20 K. No data for the density and pressure were given.

The two sets of values differ considerably and might be due to different experimental conditions, namely pressures and densities.

From the distances r_1 and r_2 it is seen that zero point energy, as expected, makes a significant contribution to Helium. On the other hand, it is obvious that superfluid Helium does not differ from ordinary Helium so far as its configurational coordinates are concerned, a fact which corroborates the theoretical prediction that superfluidity is due to condensation in momentum space.

References

- S. N. Bagchi, *Adv. Phys.*, **19**, 119 (1970).
S. N. Bagchi, *Acta. Cryst.*, **A28**, 560 (1972).
C. F. A. Beaumont and J. Reekie, *Proc. Roy. Soc. (Lond.)*, **A228**, 363 (1955).
W. L. Gordon, *et al.* from Schmidt and Tompson.
R. W. Harris and G. T. Clayton, *Phys. Rev.*, **153**, 1, 229 (1967).
R. Hosemann and S. N. Bagchi, *Acta Cryst.*, **5**, 749 (1952).
P. W. Schmidt and C. W. Tompson, X-ray scattering studies of simple fluids, in *Simple Dense Fluids*, (H. L. Frisch and Z. W. Salsburg, eds.), Academic Press, New York, 1968.