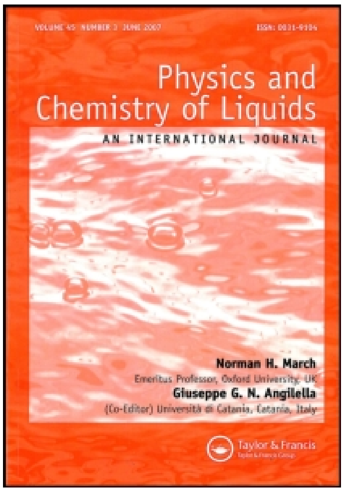

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The Use of the Coordination Number in the Interpretation of Fluid Structure

P. G. Mikolaj[a][b]; C. J. Pings[a]
[a] Division of Chemistry and Chemical Engineering California Institute of Technology, Pasadena, California [b] Department of Chemical Engineering, University of California, Santa Barbara, California

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The Use of the Coordination Number in the Interpretation of Fluid Structure*

P. G. MIKOLAJ † AND C. J. PINGS
Division of Chemistry and Chemical Engineering
California Institute of Technology, Pasadena, California

Use of radial distribution data, $g(r)$, to compute a coordination number, N_1, for liquids is discussed for four methods: A, symmetrizing the first peak in $rg(r)$; B, symmetrizing the first peak in $r^2g(r)$; C, decomposition of $r^2g(r)$ into shells; and D, computation of area to the first minimum in $r^2g(r)$. Experimental liquid structure data for argon at 13 states were used to compute N_1 for each of the four methods. Theoretical computations were also made at low densities employing a cluster integral expansion of $g(r)$. N_1 is a strong function of density, varying for method B from $N_1 = 0$ at $\varrho = 0$ to $N_1 = 6$ for $\varrho \simeq 2\,\varrho_C$ at temperatures near T_C. At $\varrho \simeq 2\,\varrho_C$ values for N_1 for methods A, B, C, and D are 5.3, 6.0, 6.6, and 7.5.

INTRODUCTION

A fundamental quantity in the description of the microscopic nature of liquids and dense gases is the radial distribution function (RDF), $g(r)$. This function represents the relative probability of finding two atoms or molecules separated by the distance r, averaged over time and over all possible configurations of the remaining atoms in the fluid system. While this quantity arises in a natural way from the formal theory of classical statistical mechanics, it does not immediately suggest a definite physical picture of the internal atomic structure, such as conveyed for solids by stipulating a type of crystal structure and unit cell dimensions.

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† Present address: Department of Chemical Engineering, University of California, Santa Barbara, California.

The study of liquid structure historically was an outgrowth of the study of solids, and many early attempts to explain and characterize liquids inevitably used the tools of solid state analysis. Because of comparable densities and intermolecular separations, liquids could easily be visualized as a rather loosely joined lattice structure. A natural consequence was the assignment to the liquid of a series of coordination numbers in the same manner as to a solid. Granted that, because of the inherent mobility of the atoms within a liquid, this concept was somewhat nebulous, it nevertheless provided a convenient mental picture of the internal atomic arrangement. As a result of this long tradition, and also because of the somewhat abstract nature of the RDF, it has been customary to compute and discuss coordination numbers when experimental or theoretical investigations and comparisons are made concerning the atomic structure of liquids and dense gases.

Although the coordination number is a holdover from solid state theory, it has a certain degree of utility in addition to merely providing a physical picture of a liquid. By considering nearest-neighbor interactions, this concept is useful in making first-order approximations to the macroscopic behavior of fluids, e.g., the process of fusion.[1,2] The coordination number has also been useful on a microscopic scale in estimating the non-additive contribution to the effective intermolecular pair potential function of non-polar liquids.[3] However, the application of this concept to liquids has also been a source of considerable confusion, notably in the case of argon. The early x-ray diffraction studies of argon[4] produced atomic distribution functions with a small sub-peak following the first coordination shell. On the basis of the structure of the solid, this sub-peak was identified as the second coordination shell in the liquid. This feature, long a subject of controversy,[5,6] has since been shown to be spurious.[7]

As a further complication, there exists no unique manner of computing the coordination numbers. Although these values are associated with the area under the peaks of the function $4\pi r^2 \varrho g(r)$ (where ϱ is the average number density), the inherent time and space average properties of $g(r)$ cause these peaks to overlap to such an extent that they can not be resolved with sufficient accuracy to give meaningful numbers. Except for peaks characteristic of intramolecular distance in polyatomic molecules, the only peak that can reasonably be termed discrete is the one corresponding to the first shell. Consequently this first coordination number or number of nearest neighbors is the only one that is generally evaluated. For this reason we shall use the term coordination number, hereafter referred to as N_1, to mean only the first coordination number in the following discussion.

It is the purpose of this paper to discuss and compare various methods presently used for computing N_1 with the hope of clarifying some of the confusion about this quantity and to offer some suggestions for possibly standardizing the computations in future investigations of fluid structure. For this purpose we shall use our recently obtained RDF data on fluid argon at 13 states in the general vicinity of the critical region.[7] In this discussion we shall concentrate generally on the noble gases and primarily on argon.

METHODS OF COMPUTING THE COORDINATION NUMBER

A survey of the published investigations of liquid structure shows that there are four commonly used methods for arriving at N_1. For identification purposes, these methods will be labeled A, B, C, and D, and will be discussed in order. Usually, although not always, these methods will result in progressively higher numerical values, i.e., $(N_1)_A <$ $< (N_1)_B$ etc. These four methods are illustrated in Fig. 1, where the function $4\,\pi r^2 \varrho g(r)$ is plotted against r. This curve is typical and represents the distribution function of liquid argon slightly below the critical temperature and at a density about 50 per cent greater than ϱ_C. For reference and comparison purposes, the location, $r_{\max}$, of the maximum of this function is shown. The leading edge of the second coordination shell (obtained by subtraction of the shaded portion from $4\,\pi r^2 \varrho g(r)$ is also shown.

METHOD A - Symmetrical $rg(r)$:

This method involves symmetrizing the first peak in the function $rg(r)$ about a radius of symmetry, r_A. N_1 is then determined from the integral

$$N_1 = \int_{r_A + \Delta r}^{r_A - \Delta r} 4\,\pi \varrho r [rg(r)]_{\text{sym}}\, dr = \int_0^{2r_A} 4\,\pi \varrho r [rg(r)]_{\text{sym}}\, dr \qquad (1)$$

The interval Δr is approximately $r_A - d$ where d is the atomic diameter.

As shown by the second equality in Eq. (1), the integration can be performed up to $2\,r_A$ since, ideally, $g(r) = 0$ for $0 \leqq r < d$, and consequently $[rg(r)]_{\text{sym}} = 0$ for $(r_A + d) < r \leqq 2\,r_A$. This method was advanced by Coulson and Rushbrooke[2] when they showed that the quantity $rg(r)$ is, for each coordination shell, symmetrical about its mean radius for any Einstein model of a liquid. This argument has also been presented in a more general manner by Viervoll[8] and by Waser and Schomaker.[9] Viervoll stresses the fact that it is $rg(r)$ that is a symmetric function and not $g(r)$ or $r^2g(r)$. Hence, he believes that interatomic distances and presumably N_1 should be based on this function. In testing their theory on the early x-ray measurements of liquid sodium,[10] Coulson and Rushbrooke were able to obtain excellent agreement with the experimental *atomic density functions*. However, their construction of symmetrical $rg(r)$ peaks was based on the existence of a small subpeak lying between the first and second coordination shells. This subsidiary peak was questioned,[5] and later experiments[11] showed it to be spurious. When this spurious subpeak is subtracted from the original experimental curve, it becomes impossible to construct symmetrical $rg(r)$ peaks that agree with the resultant experimental values.

Although this method has some theoretical foundation, to our knowledge the existence of symmetrical $rg(r)$ peaks has not yet been experimentally verified.[12] Since the $rg(r)$ radius of symmetry is less than $r_{\max}$, this method will generally produce the smallest numerical value of N_1. Its primary advantage lies in the fact that it can be accurately computed because of the clearly defined leading edge of the first peak in the RDF.

METHOD B — Symmetrical $r^2g(r)$:

This method is one of the most common ones in use and is based on the assumption that the coordination shells are symmetric about a radius, call it r_B, which defines the maximum in the function $r^2g(r)$. It is determined by evaluating the integral

$$N_1 = \int_{r_B - \Delta r}^{r_B + \Delta r} 4\,\pi\varrho\left[r^2g(r)\right]_{\text{sym}} dr = 2\int_0^{r_{\max}} 4\,\pi\varrho\left[r^2g(r)\right] dr_{\text{sym}} \qquad (2)$$

where $\Delta r \approx r_B - d$ and $r_B = r\text{max}$.

Similar to Method A, use is made of the fact that the leading edge of the first peak in $r^2g(r)$ is usually clearly defined. It likewise offers a fairly precise way of determining N_1, and, because of its unambiguity, is useful in comparing results among different investigators.

Although this method has been long and widely used, it suffers from the fact that the function $r^2g(r)$ is not really symmetric about r_B. This fact is especially noticeable in measurements made on high-density liquids near their melting points. Under these conditions the first peak is quite pronounced compared to the average density of the liquid, and its asymmetry is clearly visible. Generally speaking, the trailing edge of the first peak in $r^2g(r)$ extends beyond the symmetrical value of $r_B + \Delta r$, and any reasonable extrapolation gives a value of N_1 which is significantly larger than the symmetric $r^2g(r)$ value. This condition is physically reasonable when the microscopic behavior of the fluid particles is considered. The maximum in $r^2g(r)$ is associated with the equilibrium or most probable intermolecular separation, corresponding to the minimum of the potential energy function. In departing from this equilibrium position, the particles are severely limited in their motion toward smaller radii by the large repulsive forces of the central molecule. Although nominally bounded by the second coordination shell, the nearest neighbor particles have a good deal more latitude or freedom for moving outward toward larger radii. Consequently, it is reasonable to expect, on the average, there would be a higher number of atomic centers at larger radii, thus providing an asymmetric first coordination shell.

METHOD C — Decomposition of $4\pi r^2\varrho g(r)$ into shells:

The intuitive appeal of the argument just presented, plus the observed asymmetry of the first shell, naturally leads to an attempted decomposition of the total distribution function into its component coordination shells. While this method is probably the most objective in concept, it is the least objective in arriving at a precise value of N_1. The reason for this is that the individual shells overlap to such an extent that there is no unique way of resolving them. Thus, the N_1 may easily vary by 20 per cent depending upon how the separate coordination shells are constructed. In some cases, notably for liquids near their melting point, the first peak is sufficiently well defined so that the extrapolation of its trailing edge presents no serious problems. However, for dense gases or moderately dense liquids, such as shown in Fig. 1, the decomposition of the total distribution function into its component shells is far from obvious. Thus, the evaluation of N_1 by this method becomes a matter of the philosophy of the individual investigator. We describe one such philosophy below.

The concept of a first coordination number or number of nearest neighbors automatically implies the existence of higher coordination shells. These shells represent the average number of atomic centers to be found at some distance $\pm\delta r$ from the mean radius of the shell. While nothing is said about the shapes of the coordination shells, the continual and random motion of the individual particles dictates that they be represented by a function of r which is continuous and fairly smooth. This condition points up a deficiency of Methods A and B, at least on a conceptual basis. As shown in Fig. 1, subtraction of the first coordination shell from the total atomic distribution function will not in

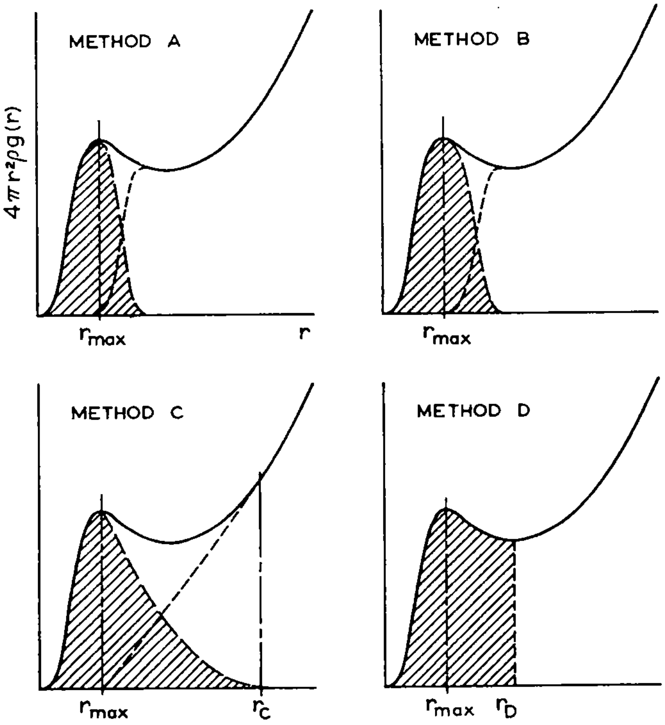

Figure 1. Plot of $4\pi r^2\rho g(r)$ *vs.* r showing the four methods for computing the coordination number.

general yield a second shell with physically meaningful properties. However, even the imposed restriction that all these hypothetical concentric shells be smoothly continuous is of little use unless some decision is made regarding their width or thickness. We use the word hypothetical because by the very nature of a fluid there is considerable interpenetration of particles between "shells" as well as migration into and out of these shells. The main problem then becomes one of rather arbitrary bookkeeping in which each particle of the fluid is to be identified with a particular coordination shell.

Recognizing the inherent random and short-range nature of fluids, it becomes a matter of pure conjecture to discuss anything beyond the first and possibly the second coordination shell. The decomposition of the total atomic distribution function can thus be limited to elucidating the overlap region between the first and second shells. To accomplish this, we take the distance $r_{\max}$, locating the maximum in $4\pi r^2 \varrho g(r)$, as being the mean radius of the first shell. We then adopt the philosophy that particles from the second shell can penetrate the first shell up to, and only up to, this distance. Any particles being at a distance less than $r_{\max}$ are counted as belonging to the first shell. Then, as shown in Fig. 1, a smooth extrapolation of the leading edge of the second shell followed by subtraction gives the outward portion of the first shell. Thus, the first shell decays to zero at $r = r_C$, and the second shell begins rising from zero at $r = r_{\max}$.

This method of treating the overlap region, while not necessarily giving a unique value of N_1, offers several advantages over other methods. Since the weak point of any decomposition-type method is the extrapolation, the most advantageous choice is obviously the one which permits the most objective extrapolation to be made. In nearly all instances, the leading edge of the second shell is more clearly defined than the trailing edge of the first shell. This fact, coupled with a clearly defined limit point makes the required extrapolation rather straight forward. While this overlap concept could be reversed, i.e., allowing the first neighbor particles to penetrate out to the mean radius of the second shell, the maximum of the second shell quite often appears only as an inflection point and its location can not be adequately defined. Thus, the decomposition method described here seems to offer a means of computing, with minimum ambiguity, a conceptually more appealing value of N_1.

METHOD D — Integration to the first minimum in $4\pi r^2 \varphi g(r)$:

While the origin of this method is not known, it appears to offer a compromise between a more realistic definition of N_1 than Methods A or B, and a more objective means of computation than Method C. As shown in Fig. 1, N_1 is determined by evaluating the integral $4\,\pi r^2 \varrho g(r)$ out to a distance, say r_D, corresponding to the first minimum on the high r side of the first peak. By so defining N_1, recognition is made of the fact that the nearest neighbor particles are more likely to stray outward from their equilibrium position than inward toward the central or reference particle. The advantage of this method is that, presumably, the characteristic distance r_D may be precisely determined, thereby giving an unambiguous value of N_1.

Method D will always result in a higher estimation of N_1 than either A or B. A comparison with Method C depends entirely upon how an isolated first peak is constructed; however, following the previously described treatment, Method D will generally produce a higher numerical value. The problem again becomes one of deciding which is the more realistic. In support of Method D, Kaplow, Strong, and Averbach[13] show that the resulting coordination number for certain liquid metal systems at their melting point is in very good agreement with the number of near neighbors in the solid. The same result was observed for liquid argon near the triple point by Gingrich and Tompson.[14] However, on the basis of our belief that there is a complete discontinuity between liquids and solids, we can not accept these fortuitous results as strong evidence for the acceptability of this method for computing N_1.

While this method has both a certain appeal and convenience, it also has some drawbacks. Its usefulness is predicated on the assumption that the characteristic radius, r_D, can be uniquely determined. For most dense liquids this is true. However, for moderately dense gases and for metals sufficiently removed from their melting point, the first minimum in $4\,\pi r^2 \varrho g(r)$ is quite broad and r_D is difficult to precisely locate. In addition, experimental $g(r)$ curves are usually plagued with spurious ripples arising from experimental errors in intensity measurements and from the subsequent Fourier analysis. These spurious features are quite often very pronounced in the general area of this first minimum, i.e., in the vicinity of r_D. These error ripples not only complicate the problem of choosing the appropriate r_D, but also produce an uncertainty in N_1 because the exact or true behavior of $g(r)$ in this region can not be ascertained.

EXPERIMENTAL COORDINATION NUMBERS FOR ARGON

To illustrate the diversity of these various methods in estimating the coordination number, we have performed the indicated computations using our recently obtained RDF data on argon.[7] Table I lists the experimental values of N_1 for each of 13 states as determined by the four previously described methods. Included in this table is our estimate of the uncertainty in N_1, arising as a result of uncertainties in $g(r)$. In Table II are listed values of the characteristic radii which were used in arriving at the experimental coordination numbers. Except for r_C, these radii have been partially smoothed by a linear correlation of the experimental values against the argon density and temperature.

Examination of the results in Table I shows that for each of the four methods there is a definite and systematic variation of N_1 with density. On the other hand, there is no obvious effect of temperature, at least over the somewhat small temperature range of our experiment. This variation of N_1 with thermodynamic state is shown in Fig. 2, using the results obtained for Method B as an example. The individual symbols in this figure represent the experimental values as given in Table 1. The results for the other three methods are similar.

This observed variation of N_1 is not entirely unexpected. From classical statistical mechanics with the usual assumptions of spherical symmetry and additive pair potentials, the RDF can be expanded in a virial series of the density with coefficients related to the Mayer cluster integrals. The resulting equation takes the form[15]

$$g(r;\varrho,T) = g_0(r;T)\left[1 + \varrho g_1(r;T) + 0\,(\varrho)^2\right] \tag{3}$$

where the temperature dependent coefficients g_0 and g_1 are also functions of the effective intermolecular pair potential function, $u(r)$.

$$g_0(r;T) = \exp\{-u(r)/kT\} \tag{4}$$

$$g_1(r;T) = \int \left[\exp\{-u(r_{13})/kT\} - 1\right]\left[\exp\{-u(r_{23})/kT\} - 1\right] dr_3 \tag{5}$$

Again using Method B as an example, substitution of Eq. (3) into Eq. (2)

TABLE I Experimental first coordination numbers for argon

Run	t(°C)	ϱ(gm/cc)	First coordination number by method			
			A	B	C	D
22	−130	0.910	4.6 ± .1	5.4 ± .1	6.2 ± .2	6.9 ± .1
23	−130	0.982	4.9 ± .1	5.8 ± .1	6.5 ± .4	7.3 ± .2
30	−125	0.910	5.0 ± .1	5.6 ± .1	6.0 ± .3	6.8 ± .2
31	−125	0.780	4.4 ± .1	4.9 ± .1	5.5 ± .2	6.0 ± .1
32	−125	0.280	1.7 ± .1	1.8 ± .1	2.2 ± .2	2.3 ± .1
33	−120	0.780	4.6 ± .2	5.1 ± .3	5.6 ± .5	6.1 ± .3
34	−120	0.536	3.3 ± .1	3.6 ± .1	4.1 ± .4	4.3 ± .2
35	−110	0.536	3.2 ± .1	3.6 ± .1	4.1 ± .4	4.2 ± .2
36	−110	0.280	1.8 ± .1	2.0 ± .1	2.2 ± .2	2.2 ± .1
37	−115	0.536	3.4 ± .2	3.7 ± .2	4.1 ± .4	4.2 ± .2
38	−110	0.780	4.7 ± .1	5.2 ± .2	5.6 ± .4	6.0 ± .2
39	−120	0.910	5.2 ± .1	5.8 ± .1	6.3 ± .4	7.0 ± .2
40	−125	0.982	5.6 ± .1	6.2 ± .1	6.7 ± .2	7.5 ± .1

TABLE II

Characteristic radii used in determining experimental coordination numbers

Run	r_A (Å) [a]	r_B (Å) [b]	r_C (Å) [c]	r_D (Å) [d]
22	3.86	3.96	6.0	4.92
23	3.85	3.95	6.2	4.92
30	3.87	3.97	5.8	4.92
31	3.88	3.98	6.1	4.91
32	3.90	4.00	6.1	4.87
33	3.90	4.00	6.1	4.91
34	3.91	4.00	6.1	4.89
35	3.94	4.04	6.3	4.88
36	3.95	4.05	6.4	4.86
37	3.92	4.02	6.1	4.89
38	3.93	4.03	6.1	4.90
39	3.89	3.99	6.0	4.91
40	3.87	3.97	6.0	4.92

[a] r_A is the location of the maximum in $rg(r)$

[b] r_B is the location of the maximum in $r^2g(r)$

[c] r_C locates the high r limit of the isolated first shell in Method C

[d] r_D is the location of the first minimum in $r^2g(r)$

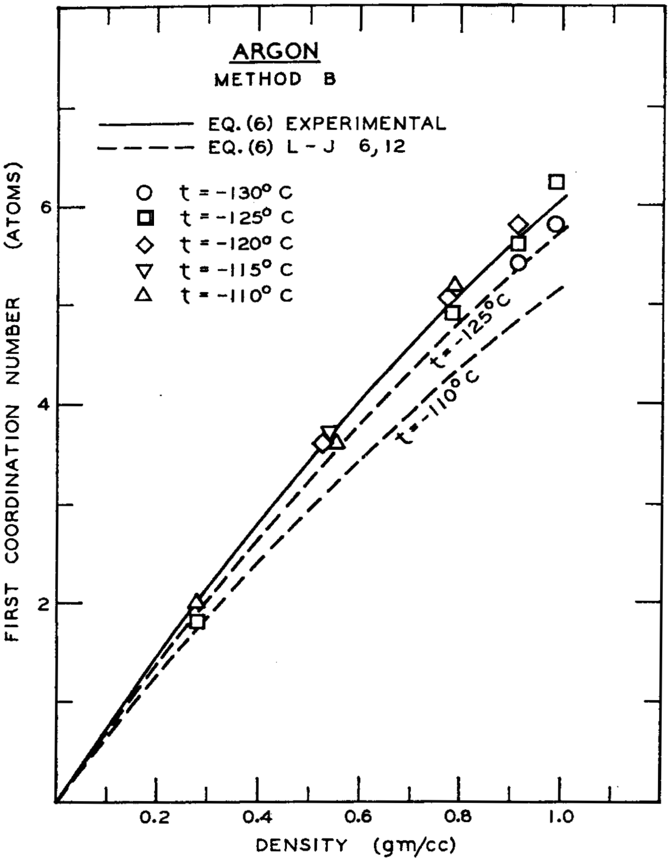

Figure 2. The effect of density on the first coordination number of argon as determined by Method B. The symbols show the experimental values and the solid curve represents a second-order virial expansion fitted to the data points. The dashed curves represent a theoretical model using a Lennard-Jones 6–12 potential function.

gives a corresponding density expansion for the first coordination number

$$N_1 = \eta_1(T)\,\varrho + \eta_2(T)\,\varrho^2 + 0(\varrho^3) \tag{6}$$

with the coefficients given by the equations

$$\eta_1(T) = 8\,\pi \int_0^{r_B} r^2 g_0(r;\,T)\,dr \tag{7}$$

$$\eta_2(\mathrm{T}) = 8\pi \int_0^{r_B} r^2 g_0(r;\,\mathrm{T}) g_1(r;\,T)\,dr \tag{8}$$

where r_B is the location of the first maximum of the function $r^2 g(r)$.

Following the form of Eq. (6), the experimental data were fitted by least squares to a second degree polynomial in density. Since there was no observable temperature variation of the data, η_1 and η_2 were assumed to be constants. The resulting correlation for Method B is shown as the solid curve in Fig. 2. In Table III are listed numerical values of the coefficients for each method as well as the mean square deviation (MSD) in atoms. Values of the MSD show that the data are well represented by a second degree polynomial. A third degree function was also tried, but gave essentially no improvement in the fit.

TABLE III Coefficients in the virial expansion of the first coordination number

		Method			
		A	B	C	D
	η_1*	7.07	7.54	8.59	8.28
Experimental	η_2**	−1.73	−1.46	−1.92	−0.74
	MSD	0.22	0.17	0.14	0.10
Theoretical	η_1	5.37	6.53	8.99	7.11
$L-J$ 6–12	η_2	−0.91	−1.36	−1.82	0.76
$t = -110$°C	MSD	0.02	0.01	0.01	0.03
Theoretical	η_1	5.69	7.20	9.21	8.08
$L-J$ 6–12	η_2	−0.74	−1.46	−1.17	1.00
$t = -125$°C	MSD	0.02	0.03	0.04	0.03

* η_1 in units of atoms — $(\mathrm{gm/cc})^{-1}$
** η_2 in units of atoms — $(\mathrm{gm/cc})^{-2}$
† MSD is the mean square deviation in atoms

The virial expansion as given by Eq. (6) may be used to gain further insight into the behavior of the first coordination number. The temperature coefficients η are related to the effective manybody interactions within the fluid. Truncation of this series after the ϱ^2 term is tantamount to neglecting all but the two and three particle interactions. While this condition is reasonable at low densities, it is certainly not realistic at higher densities. Nevertheless, this approximation should provide some indication as to the effect of temperature on N_1. Following this reasoning we have evaluated the three particle interaction integral of Eq. (5) and have computed "theoretical" coordination numbers. These computations were made with a Lennard-Jones 6–12 potential function for argon using parameters $\varepsilon/k = 119.8$°K and $\sigma = 3.405$ Å. Two isotherms were studied, -110°C and -125°C, and coordination numbers were evaluated at the five densities studied in the experimental work.[16] These theoretical results were correlated by least squares techniques according to Eq. (6), and the resulting values of $\eta_1 (T)$ and $\eta_2 (T)$ are listed in Table III. Using Method B again as an illustration, the theoretical coordination numbers for a L-J 6–12 potential are plotted in Fig. 2 as the dashed curves.

In view of the severe limitations of the theoretical models, there is surprising agreement between the experimental values and those predicted from Eq. (6) with a L-J potential function. Also in agreement with the experimental results is the rather small temperature effect. The other three methods showed a similar behavior, with the theoretical coordination numbers varying by about 10 per cent over the indicated temperature range. For methods A and B, the theoretical coordination numbers were slightly lower than the experimental values while for Methods C and D they were slightly higher.

A summary of our experimental results is shown in Fig. 3, where correlated values of the experimental first coordination number are plotted against the sample density for each of the four methods. We also show in this figure the results obtained from previous investigations of liquid argon and indicate the method used in arriving at these values. Both the neutron work of Henshaw[17] and the x-ray work of Gingrich and Tompson[14] were done near the triple point (-189.4°C and $\varrho = 1.41$ gm/cc). The other values of Eisenstein and Gingrich[4] correspond to measurements made along the vapor—liquid coexistence curve. These points are displaced slightly on the graph in order to distinguish among them.

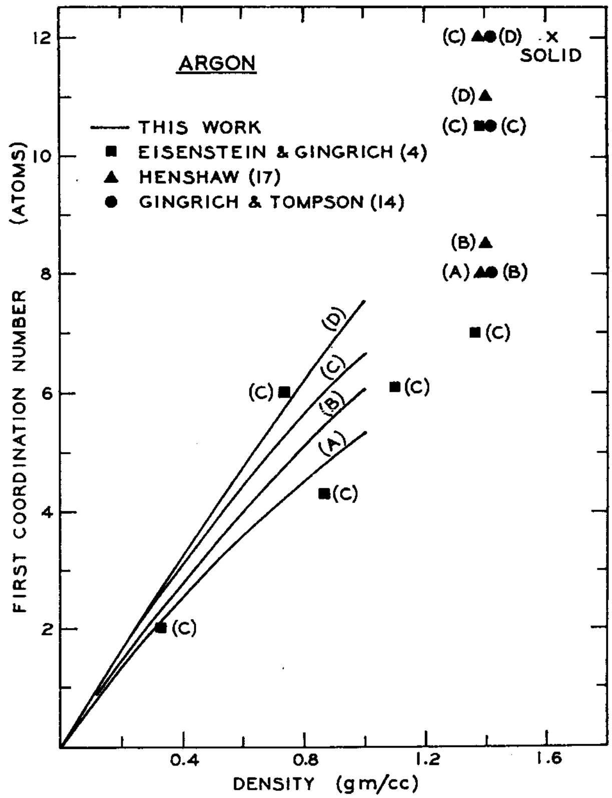

Figure 3. Summary of the experimental first coordination number of argon. The solid curves labelled A, B, C, and D represent the correlated experimental results of this work. The symbols correspond to the previous measurements of other investigators and are also identified according to the method used in the computation of N_1.

DISCUSSION

From the results presented here, several statements may be made regarding the applicability of the coordination number as a means of interpreting fluid structure. In the first place, it is clear that the specification of a liquid state coordination number is meaningless unless the method by which it has been evaluated is clearly stated. While this statement might seem to be obvious, it is also apparent that this basic fact is quite often overlooked. In a recent survey[18] of the existing RDF data for liquid mercury near room temperature, the first coordination number, as reported by fourteen different investigators, varied from about 6 to 12. Out of all these separate studies, which covered the period from 1930 to 1964, only one investigator specifically defined the method by which the coordination number had been determined.

Secondly, unlike crystalline solids, the coordination number of a liquid is not constant but varies markedly with thermodynamic state. For noble gases below the critical temperature, N_1 will vary from about 3.7 ± 0.5 at the critical point to about 10 ± 2 at the triple point, depending on the method used; for the more general fluid or dense gas state, it will vary from zero at zero density to a value possibly larger than that of the solid at extremely high pressures. The predominant factor in determining the variation of the coordination number appears to be the density, with temperature having a smaller effect. This behavior is plausible on the physical basis that an increase in temperature tends to impart a higher degree of mobility to the fluid particles, thereby broadening, and perhaps shifting, the first peak in $g(r)$. While the probability of locating the exact position of each particle is reduced, a restriction of constant density fixes the effective or average volume of each particle. Thus, an integration over the volume which is available to the first shell should result in a relatively constant number of nearest neighbors. This is in agreement with a recent study by Melrose,[19] who estimated that the coordination number varied by only 15 per cent over a reduced temperature range of 1.0 to 1.5.

One of the major causes for the nebulosity associated with the coordination number seems to be the uncertainty as to which method gives the "best" or most realistic value. It is our opinion that this question is irrelevant and that too much emphasis has been placed on giving a literal interpretation to this quantity. For reasons discussed earlier, the concept of a coordination number suffers a drastic loss in the translation from solid state language to that of the liquid state. Nevertheless, it is also apparent that this quantity offers a means of summarizing some of the characteristics of the structure of a fluid. For example, in describing the vaporization of argon at −125°C, it is convenient to state that the coordination number changes from about 5 atoms in the saturated liquid to about 2 atoms in the saturated vapor. While this piece of information does not replace a detailed description of the corresponding changes in the RDF, it is helpful in visualizing the structural changes which take place. In view of the hypothetical nature of the coordination number when applied to liquids, it seems questionable whether a change from 6.0 to 2.3 atoms according to Method D conveys any more or any less information than a change from 4.9 to 1.8 atoms according to Method B.

We would like to suggest that the coordination number is a useful structural parameter, but is essentially devoid of any absolute meaning. While it might be helpful to coin a new name for this parameter in order to avoid ambiguity, it appears that the term "coordination number" is too deeply entrenched in the history of fluid state theory. The question of which method should be used to compute this quantity obviously has no rigorous answer. Therefore, we again stress the fact that any computation of a liquid state coordination number should be accompanied by a clearly defined explanation of the method used.

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