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Analytical formula for the radial distribution function

Witold Brostow
Département de Chimie, Université de Montréal, Montréal, Québec H3C 3V1, Canada

Jerzy S. Sochanski
Centre de Calcul, Université du Québec, Trois-Rivières, Québec G9A 5H7, Canada

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The most accurate experimental radial-distribution-function data, obtained by thermal-neutron scattering and x-ray scattering in liquids, have been considered. A number of analytical equations for the radial distribution function g as a function of the interparticle separation R have been studied. The formula for $g(R)$ finally chosen gives completely satisfactory agreement with the experimental data, and also with some Monte Carlo simulations and with theoretical predictions of the Percus-Yevick type. It is expected that the same formula will be also applicable to at least some of the diffractometric data for amorphous solids.

I. INTRODUCTION

The radial distribution function $g(R)$, where R is the intermolecular separation, contains essential information about the equilibrium properties of a liquid.[1,2] Usually measurements of the intensity of either slow-neutron or x-ray scattering are made; the diffractometric data are expressed in terms of the structure factors. The Fourier transforming of the structure factors then produces $g(R)$. False undulations of $g(R)$ often appear for small values of R; thus caution must be exercised in the transformation procedure.[3] In either case, one typically winds up with a tabulated set of $g(R)$ values.

We may represent relations between the equilibrium properties and the radial distribution function by

$$F=\int_0^\infty f(R)g(R)\,dR+f_0. \tag{1}$$

Here F stands for an equilibrium property such as the configurational energy, the macroscopic pressure, the average number of nearest neighbors of a molecule in the bulk of the liquid phase, the isothermal compressibility, and so on. The form of $f(R)$ and the value of f_0 depend on the choice of the quantity F; f_0 is either a constant or an explicit function of temperature T and/or density ρ.

Equation (1) suggests that an analytical equation for $g(R)$, as contrasted to the tabulated values of this function, would be highly desirable. Attempts in this direction have been made before, but the problem was found quite difficult. The main peak of $g(R)$ is as a rule highly asymmetrical and widely different in both size and shape from the subsequent peaks. In this context, the objective of the present work was to produce an analytical equation for the radial distribution function, working in the entire range of R.

II. FORMULATION AND CALCULATIONS

Important work on the present problem has been done by Franchetti,[4,5] and we have considered first his Eq. (2.1) in Ref. 5. Franchetti expresses $g(R)$ in terms of coordination number Z_i and radii of consecutive shells around an atom placed at $R=0$; rather arbitrarily, he takes $Z_i=12$. Calculated values of $g(R)$ for argon and zinc show reasonable agreement with the respective experimental data for larger values of R, but are unacceptable in the region of the main peak. In our calculations, we have modified the Franchetti equation somewhat, treating the coordination numbers and the shell radii as adjustable parameters. The results were similar to his own, however, in that the calculated main peak was always too flat and too broad.

Subsequently, we have tried a variety of equations which we do not propose to describe here. The equation which we have finally adopted, and which gives the best results, represents a sum of three terms,

$$g(R)=g_a(R)+g_b(R)+g_c(R), \tag{2}$$

the terms being defined by

$$g_a=0,\quad R\leqslant B_6$$
$$g_a=\frac{B_5}{R-B_6}\exp\{-B_7[\ln(R-B_6)+B_8-10]^2\},\quad R>B_6 \tag{3a}$$

$$g_b=\exp[-(R-B_1)^2/B_2],\quad R\leqslant B_1$$
$$g_b=1,\quad R\geqslant B_1 \tag{3b}$$

$$g_c=0,\quad R\leqslant B_1-\tfrac{1}{4}B_4$$
$$g_c=\frac{\sin[2\pi(R-B_1+0.25B_4)/B_4]}{B_3-10+(B_9-4)R^2+(B_{10}-0.01)R^4},\quad R>B_1-\tfrac{1}{4}B_4. \tag{3c}$$

We note that Eqs. (3) could be slightly simplified by introducing, e.g., $B_3' = B_3 - 10$, $B_8' = B_8 - 10$, etc. We have used a computer subprogram which searched for values of the B_i parameters and which contained a condition that all unknown parameters be positive. This is the reason for writing Eqs. (3) the way we did; the form given here is the one actually used in the computations.

Let us now explain the three terms in turn. The g_a term takes care of the main peak; at $R = B_6$ we have the point often referred to as the first minimum of $g(R)$. The g_b term serves for connection of the main peak with the sinusoidal tail g_c. As for the latter, its first maximum is evidently at B_1; this point is typically fairly close to the second maximum $R_{\text{II}_{\max}}$ of $g(R)$, such that $R_{\text{II}_{\max}} \approx B_1$, and the starting value for B_1 in the computations is chosen accordingly. Similarly, an approximate distance between two extrema of the same kind suggests the starting value for the sinusoidal period parameter B_4.

The parameters B_i have been obtained using a nonlinear least-squares curve-fitting program on a CYBER 74 computer. The program (NLWOOD) is, along with other computer procedures, performing essentially the same task, discussed in detail by Cuthbert and Woods.[6] The program produces an optimized set of B_i parameters, a number of statistical parameters including values of Student's t function for each of the B_i, and the residual root-mean-square deviation σ for the entire curve. Subsequently, the program ZXPOWL (available from International Mathematical and Statistical Libraries, Houston) has furnished us with locations and values of all maxima and minima of the radial distribution function as given by the fitted analytical formula.

III. RESULTS

Our calculations have been based on recent and sufficiently accurate $g(R)$ data. Inspecting the values obtained one notices, first of all, high values of Student's t parameters, running in many cases into several hundreds. Since an analytical equation is considered as acceptable when t values for fitted parameters are all higher than 2, the t values here testify well to the soundness of our formula.

The calculations made are summarized in two tables. Table I characterizes the data used (system, temperature, density or pressure, literature source) and quality of the fit as represented by σ; it also contains locations of the main maximum of each $g(R)$ curve as $R_{\max}$ and $g_{\max}$. Table II contains sets of B_i parameters; consecutive numbers in the first column refer to the respective sets of data as characterized in Table I.

IV. DISCUSSION

Let us briefly consider now in turn all sets of data and the results obtained. The first set involves the neutron scattering data for Ar of Yarnell and his colleagues[7]; there appears to be a general consensus that these are the most accurate experimental values of $g(R)$ now available. There are 400 points, covering the R range up to 2.724 nm. All of equations we have used, from the Franchetti formula up to Eq. (2), have been tried on this set of data; only when a satisfactory agreement had been obtained did we pass to other systems.

While these data are relatively the best, and in spite of a smoothing procedure used by Yarnell *et al.*,[7] their $g(R)$ curve still contains some oscillations at small values of R. Eliminating a number of experimental points in this range would produce a distinct improvement in our value of the residual deviation σ, particularly since some of the experiment-derived $g(R)$ values are negative. Any procedure for excluding a number of points, such as eliminating all negative g values, or else eliminating all data below a certain value of R, would necessarily be somehow subjective and arbitrary. We have therefore decided to present the value of σ which corresponds to all the experimental points available. The same applies to all subsequent systems.

A word on the location of the main $g(R)$ peak at 85 K might be in order. Earlier interaction potentials $u(R)$ for Ar assumed that the potential-energy minimum $u_{\min}/k$, where k is the Boltzmann constant, is $\simeq -120$K,while the minimum is located at $R_{\min} \simeq 0.38$ nm. Differences between various potentials were minor ($u_{\min}/k = -119.4$ K, or -119.8 K, etc.) until Guggenheim and McGlashan[8] demonstrated that $u_{\min}/k$ should be of the order of -140 K. Proposals of $u(R)$ potentials made since then have shifted accordingly, but $R_{\min} \simeq 0.38$ nm has remained.

It is a well-known fact among the liquid-state experimentalists that the principal peak of $g(R)$ occurs at a position close to but not identical to the principal minimum of $u(R)$ (cf. Egelstaff,[2] Chap. 2). Since the experiments of Yarnell *et al.* have been made at a temperature not far from the triple point of argon and we find from their data that $g_{\max}$ is located at $\simeq 0.37$ nm rather than at 0.38 nm, we expect that the future proposals of $u(R)$ for Ar will take this fact into consideration. Incidentally, one of us[9] has found $R_{\min}(u_{\min})$ using the Jonah equation[10] and the same $g(R)$ data from Ref. 7. The Jonah procedure is hardly exact; the result obtained,[9] however, $R_{\min}(u_{\min}) = 0.3728 \pm 0.0003$ nm, is quite acceptable from the point of view of the value of $R_{\max}(g_{\max})$ now found.

Let us now consider other available $g(R)$ data for Ar. Page[11] has made neutron scattering measurements at 84.5 K. Since his experimental temperature is so close to that of Yarnell *et al.*, and since the latter report[7] that the agreement between their results and his results is very good, there was little point in our dealing separately with Page's results. Furthermore, there are x-ray scattering results, notably those of Mikolaj and Pings.[12] New results from the same laboratory,[13] however, are considered to be of higher quality,[14] and we have performed calculations for the data of Kirstein and Pings.[13] The results are presented in the tables as systems 2–12. "Table 5.C," etc., refers to the respective table in the thesis of Kirstein. Since for each of the thermodynamic states (defined by temperature and density) studied Kirstein and Pings have made at least two independent series of measurements, we can make comparisons of the resulting values of $R_{\max}$ and $g_{\max}$. When one also takes into consideration the respective values of σ, it appears that our Eq. (2) describes the $g(R)$ values within the limits of experimental accuracy.

For ^{4}He, relatively highly accurate neutron diffraction measurements have been made by Mozer and his colleagues[15] for several thermodynamic states. The results of Mozer *et al.* are presented in the form of the structure factors, and Mountain and Ravechė[16] have calculated therefrom the $g(R)$ values. In our computations we have thus used the values tabulated by Mountain and Ravechė. As can be seen from the respective values of σ in Table I, the experiments are indeed accurate, and our Eq. (2) represents them in a satisfactory way.

Neutron diffraction studies for liquid neon[17] have been made in the same laboratory as for helium. DeGraaf and Mozer[17] do not report the numerical values of $g(R)$, but the respective tabulated data have been obtained from Mozer.[18] Their experiments were performed at a single temperature, but under three different pressures; the agreement with the calculated values is as good for Ne as it has been for ^{4}He.

Finally, we have considered experimental $g(R)$ data for metals. Among these, the x-ray data for sodium of Greenfield, Wellendorf, and Wiser[19] seem to stand out because of their accuracy (cf. p. 127 in Faber[20]). Typically again, Greenfield *et al.* tabulate the structure factors but not the radial-distribution-function values. Murphy and Klein,[21] assuming an ion-ion interaction potential $u(R)$ for Na, have performed Monte Carlo computer simulations

TABLE I. Systems studied, values of σ, and locations of the main peak of $g(R)$.

No.	System	Ref.	σ	$R_{\max}$ (nm)	$g_{\max}$
1	Ar; 85.0 K, vapor-liquid equilibrium	7	0.023	0.3689	2.961
2	Ar; 127.0 K, 1.116 g cm^{-3}	13, Table 5.C	0.028	0.3831	2.143
3	Ar; 127.0 K, 1.116 g cm^{-3}	13, Table 5.E	0.028	0.3780	2.074
4	Ar; 127.0 K, 1.098 g cm^{-3}	13, Table 5.F	0.037	0.3779	2.143
5	Ar; 127.0 K, 1.098 g cm^{-3}	13, Table 5.I	0.029	0.3787	2.130
6	Ar; 127.0 K, 1.135 g cm^{-3}	13, Table 5.J	0.027	0.3812	2.069
7	Ar; 127.0 K, 1.135 g cm^{-3}	13, Table 5.K	0.025	0.3785	2.118
8	Ar; 133.0 K, 1.054 g cm^{-3}	13, Table 5.D	0.045	0.3827	2.144
9	Ar; 133.0 K, 1.054 g cm^{-3}	13, Table 5.G	0.027	0.3798	2.060
10	Ar; 143.0 K, 0.910 g cm^{-3}	13, Table 5.A	0.028	0.3845	2.003
11	Ar; 143.0 K, 0.910 g cm^{-3}	13, Table 5.H	0.040	0.3713	2.006
12	Ar; 143.0 K, 0.910 g cm^{-3}	13, Table 5.B	0.035	0.3794	1.971
13	^{4}He; 1.860 K, 0.44 J cm^{-3}	15, 16	0.018	0.3474	1.435
14	^{4}He; 2.050 K, 0.44 J cm^{-3}	15, 16	0.010	0.3507	1.414
15	^{4}He; 2.130 K, 0.37 J cm^{-3}	15, 16	0.022	0.3497	1.458
16	^{4}He; 2.140 K, 0.37 J cm^{-3}	15, 16	0.018	0.3489	1.459
17	^{4}He; 2.300 K, 0.38 J cm^{-3}	15, 16	0.017	0.3490	1.458
18	^{4}He; 2.840 K, 0.54 J cm^{-3}	15, 16	0.017	0.3478	1.455
19	^{4}He; 2.020 K, 0.66 J cm^{-3}	15, 16	0.012	0.3490	1.421
20	^{4}He; 2.860 K, 0.79 J cm^{-3}	15, 16	0.012	0.3490	1.429
21	^{4}He; 1.940 K, 1.18 J cm^{-3}	15, 16	0.011	0.3461	1.434
22	^{4}He; 2.860 K, 1.27 J cm^{-3}	15, 16	0.008	0.3465	1.447
23	Ne; 35.05 K, 2.17 J cm^{-3}	17, 18	0.014	0.3088	2.248
24	Ne; 35.05 K, 8.00 J cm^{-3}	17, 18	0.015	0.3076	2.315
25	Ne; 35.05 K, 14.18 J cm^{-3}	17, 18	0.017	0.3068	2.357
26	Na; 273.2 K, the Percus-Yevick equation	21	0.027	0.3575	2.606
27	Na; 373.2 K, the Percus-Yevick equation	21	0.018	0.3689	2.386
28	Na; 273.2 K, Monte-Carlo simulation	21	0.020	0.3656	2.504
29	Na; 373.2 K, Monte Carlo simulation	21	0.015	0.3689	2.961

for the two experimental temperatures of Greenfield *et al.* The simulated structure factors are in what Murphy and Klein call excellent agreement with the x-ray diffraction data in Ref. 19. In view of this, we have performed calculations using the $g(R)$ data for Na obtained by the Monte Carlo method. Furthermore, Murphy and Klein give two other sets of $g(R)$ data, again for experimental temperatures of Greenfield *et al.*, but obtained using the Percus-Yevick approximation; we have included these data in our calculations also. We have found that the $g(R)$ curves for sodium produced by computer simulation as well as those predicted theoretically using the Percus-Yevick formula are also well represented by our equation.

In conclusion, we expect our $g(R)$ formula to be applicable to any "decent" liquid. A notable exception, where experimental $g(R)$ curves are available but are so involved that an equation more complex than ours may be needed, is, of course, water.[22,23]

While we have not made any calculations for solid amorphous materials, our equations might be worth trying for them also. Amorphous metals are known to have structures highly resembling the respective liquid phases, particularly when deposited as not-too-thin films (cf. Faber, Ref. 20, p. 274). Amorphous water will be an exception again, as is apparent from an acceptable explanation of the behavior of water which, at last, we are about to receive.[23] On the other hand, amorphous semiconductors and organic polymers represent further classes of likely candidates for the applicability of our equation. Among the latter, we have several industrially important amorphous materials, such as atactic polystyrene, polymethylmethacrylate, and polyvinyl acetate, which from the point of view of their diffractometric characteristics are indeed liquidlike.[24]

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TABLE II. B_i parameters in the radial-distribution-function equation, rounded to four decimal points.

Data set No.	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	B_9	$10^2 B_{10}$
1	6.9764	4.1589	11.5344	3.2451	1.9159	3.1026	1.9270	10.2802	4.0100	1.0640
2	6.9980	5.3964	119.2140	4.6352	3.2534	2.2412	6.2382	9.4678	0.6703	3.6684
3	7.1613	6.2638	25.4041	3.9655	2.6698	2.4491	4.0472	9.6055	3.5648	1.5654
4	7.0447	5.7820	120.4440	4.2895	2.5651	2.5511	3.8628	9.6798	0.5991	3.7711
5	7.1070	6.1477	110.4721	4.1516	2.6319	2.5095	4.0817	9.6468	0.9273	3.4880
6	7.1348	5.9514	54.1881	3.7948	2.9754	2.3127	5.0462	9.5094	2.5952	2.3142
7	7.0920	5.9497	67.1752	3.9531	2.8743	2.3751	4.7950	9.5652	2.2125	2.5841
8	6.7976	5.1424	142.6840	5.7280	3.2732	2.1988	7.3241	9.4561	0.0669	4.0449
9	7.0904	6.7350	136.2320	4.1196	2.6526	2.4291	4.5003	9.5908	0.0923	4.1771
10	7.1832	6.7121	39.3706	4.6113	2.5132	2.5245	3.8272	9.6091	3.2312	1.8174
11	7.3085	6.1605	18.1966	3.6838	1.8475	2.8607	1.5506	9.8587	3.7368	1.7178
12	7.1985	7.8192	55.6103	4.1737	2.0737	2.6802	2.9346	9.7431	2.7338	2.2591
13	6.7851	3.5930	164.4690	3.1766	2.8122	1.5702	3.1205	9.2149	0.2364	3.6786
14	6.7645	4.5025	94.1455	3.3414	3.0800	1.2461	4.5708	9.1004	1.8833	2.8400
15	6.7663	3.1709	97.5872	3.2037	2.9516	1.5484	3.2627	9.1947	2.0055	2.4841
16	6.7767	3.2132	140.9130	3.2069	2.8653	1.6076	3.0693	9.2203	0.8183	3.2538
17	6.7719	3.3398	94.7252	3.1972	2.8948	1.5713	3.2237	9.2098	2.0663	2.4516
18	6.7995	3.4725	110.9951	3.1448	2.8013	1.6233	3.0098	9.2334	1.5730	2.7979
19	6.7504	3.7054	111.8260	3.2561	3.0882	1.3248	3.9579	9.1214	1.5760	2.8526
20	6.7505	3.6123	90.1885	3.2340	3.1213	1.3239	3.9720	9.1199	2.1447	2.4530
21	6.6507	3.4728	86.3081	3.2756	3.2144	1.2246	4.3746	9.0988	2.1558	2.5212
22	6.6357	3.3448	70.2511	3.2538	3.2725	1.2157	4.5000	9.0950	2.5537	2.2540
23	5.9223	3.9113	19.5204	2.8261	1.6494	2.3833	2.2306	10.1390	3.6384	1.7709
24	5.8910	3.8648	19.4890	2.7838	1.6544	2.3887	2.2992	10.1704	3.6422	1.7098
25	5.8688	3.7182	14.4968	2.7459	1.6990	2.3755	2.3948	10.1704	3.8731	1.4245
26	6.7142	5.3526	38.6855	3.2661	2.5901	2.5642	4.6364	9.8898	3.0000	2.0017
27	6.7006	5.0163	38.7283	3.3429	2.5901	2.4583	4.4479	9.8017	3.0000	2.0255
28	6.7118	2.9270	30.2308	3.8040	2.9605	2.5170	4.2754	9.7575	3.3485	1.6277
29	6.7177	3.0182	32.3613	3.8247	2.9616	2.4017	4.2292	9.6742	3.2970	1.6578

[1] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience, New York, 1965).

[2] P. A. Egelstaff, *An Introduction to the Liquid State* (Academic, London, 1967).

[3] C. J. Pings, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (North-Holland, Amsterdam, 1968).

[4] S. Franchetti, Nuovo Cimento B 55, 335 (1968).

[5] S. Franchetti, Nuovo Cimento B 10, 211 (1972).

[6] D. Cuthbert and F. S. Woods, *Fitting Equations to Data* (Wiley, New York, 1971).

[7] J. L. Yarnell, M. J. Katz, R. G. Wenzel, and S. H. Koenig, Phys. Rev. A 7, 2130 (1973).

[8] E. A. Guggenheim and M. L. McGlashan, Proc. R. Soc. A 255, 456 (1960).

[9] W. Brostow, Chem. Phys. Lett. 35, 387 (1975).

[10] D. A. Jonah, Mol. Phys. 21, 755 (1971).

[11] D. I. Page, Harwell Report No. AERE-R6828 (unpublished).

[12] P. G. Mikolaj and C. J. Pings, J. Chem. Phys. 46, 1401 (1967).

[13] B. Kirstein, Ph.D. thesis (California Institute of Technology, 1972) (unpublished); B. Kirstein and C. J. Pings (unpublished).

[14] C. J. Pings (private communication).

[15] B. Mozer, L. A. De Graaf, and B. Le Neindre, Phys. Rev. A 9, 448 (1974).

[16] R. D. Mountain and H. J. Raveché, J. Res. Natl. Bur. Stand. (U. S.) A 77, 725 (1973).

[17] L. A. De Graaf and B. Mozer, J. Chem. Phys. 55, 4967 (1971).

[18] B. Mozer (private communication).

[19] A. J. Greenfield, J. Wellendorf, and N. Wiser, Phys. Rev. A 4, 1607 (1971).

[20] T. E. Faber, *An Introduction to the Theory of Liquid Metals* (Cambridge U. P., 1972).

[21] R. D. Murphy and M. L. Klein, Phys. Rev. A 8, 2640 (1973).

[22] A. H. Narten and H. A. Levy, J. Chem. Phys. 55, 2263 (1971); C. G. Venkatesh, S. A. Rice, and A. H. Narten, Science 186, 927 (1974).

[23] S. A. Rice, Top. Curr. Chem. (to be published).

[24] G. Champetier and L. Monnerie, *Introduction à la chimie macromolêculaire* (Masson, Paris, 1969), p. 402.