Fluctuations in the Radial Distribution Function for Simple Liquids

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Radial fluctuation functions which convey information about liquid microstructure are defined, determined from computer generated configurations, and discussed.

The equilibrium microstructure of a fluid may only be described exactly in terms of a complete set of n-body atomic distribution functions, where n is 1, 2, 3, ..., N, and N is the total number of particles in the system. The higher order functions, i. e. $n > 2$, are complex and practically inaccessible but considerable qualitative information can already be derived from studies of the mean radial occupation function $n(r)$ defined as the average number of atoms in a sphere of radius r centred on a particular atom. The function for a perfect gas of non-interacting particles is

$$n^*(r) = \tfrac{4}{3}\,\pi\, r^3\, \varrho \qquad (1)$$

where ϱ is the number density N/V. Differentiation of $n(r)$ with respect to radius and normalisation relative to the bulk density gives the radial distribution function

$$g(r) = [\mathrm{d}n(r)/\mathrm{d}r]/[\mathrm{d}n^*(r)/\mathrm{d}r]\,. \qquad (2)$$

Neutron and X-ray scattering experiments have been widely used to obtain radial distribution functions for a variety of liquids[1]. For simple liquids such as the condensed group 0 elements, computer simulation methods can be used to derive information about liquid structure[2]. Extensive $g(r)$ data obtained from molecular dynamics (MD) calculations for liquid Lennard-Jones molecules are tabulated in the literature[3]. The latter techniques have an advantage over the former in that they may yield quantitative values for any requisite configurational average to a comparatively high level of accuracy. In principle, the average liquid structure could be determined exactly but even if this were practical it would be difficult to interpret the data for the multiplet distribution functions. The triplet distribution itself poses a formidable problem of presentation. Information which is contained in the pair distribution function, however, may be extended by studying not only the mean radial occupation function $n(r)$ but also fluctuations about the mean.

The "term coordination number" has been extensively used to describe local structure in liquids[4]. A mean first-coordination number may be defined as the value of $n(r)$ when $g(r)$ displays its first minimum, although alternative definitions have been suggested and discussed[4]. Knowledge acquired through studying coordination numbers, or more generally $n(r)$ the mean radial occupation function, is limited in that it contains no information regarding fluctuations of, and distributions around, the mean value. It is appropriate to define two further functions as

$$f(r) = \langle (\Delta n^2)_r{}^{1/2} \rangle / n(r) \qquad (3)$$

and

$$w(r) = \langle (\Delta n^2)_r \rangle / n^*(r) \qquad (4)$$

where $\langle (\Delta n^2)_r \rangle$ is the mean squared fluctuation around the mean radial occupation function $n(r)$. Values of $f(r)$ are therefore standard deviations of radial occupation numbers. The normalised variance $w(r)$ is a more useful function and is related to the isothermal compressibility at large r by the familiar statistical mechanical expression for fluctuations in density, which gives

$$w(r \to \infty) = -\frac{N\,k\,T}{V^2}\left(\frac{\partial V}{\partial p}\right)_T. \qquad (5)$$

Numerical Procedure

Chains of configurations typical of a real simple liquid were generated by the Monte Carlo method of Metropolis et al. (1953) which has more recently

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[1] See e. g. P. A. Egelstaff, Introduction to the Liquid State, Academic Press, London 1967.

[2] I. R. McDonald and K. Singer, Quart. Rev. **24**, 238 [1970].

[3] L. Verlet, Phys. Rev. **165**, 201 [1968].

[4] P. G. Mikolaj and C. J. Pings, J. Phys. Chem. Liquids **1**, 93 [1968].

been described in detail elsewhere[5]. The pair potential employed is a Lennard-Jones function

$$\Phi_{ij} = 4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

with the parameters, $\varepsilon/k_\beta = 117.2$ K and $\sigma = 3.405$ Å, having previously been found to adequately reproduce the experimental internal energy and pressure of argon over the entire liquid range[2]. Moreover, the radial distribution functions obtained using the Lennard-Jones function are also found to be in good agreement with the experimental curves from X-ray scattering measurements[3].

The functions $g(r)$, $f(r)$ and $w(r)$ are calculated from two basic histograms: the mean radial occupation number $n(r-\Delta r, r+\Delta r)$ and the mean squared radial occupation number $n^2(r-\Delta r, r+\Delta r)$. These histograms incorporate a double average, firstly over the N particles in the basic cube and secondly over a large number of configurations. In order to minimize residual fluctuation errors, the configurations chosen for analysis were selected from widely spaced intervals (every 2000 steps) in the MC chain. The value of Δr is 0.05 Å. Having obtained the basic data on termination of the MC chain, Equations (2), (3) and (4) are applied in a straightforward manner to calculate $g(r)$, $f(r)$ and $w(r)$ respectively. All the calculations were performed on a basic cubic system containing 216 particles and subjected to the usual periodic boundary conditions.

Results are reported for four V-T points chosen so as to represent states of liquid argon on the liquid-vapour coexistence curve. The reduced temperatures of the points are $T/\varepsilon = 0.75$, 0.9, 1.05 and 1.2, broadly scanning the orthobaric range from the triple point (0.72) to the critical point (∼1.3) for the Lennard-Jones system.

Results and Discussion

Table 1 lists the values of $n(r)$ and $f(r)$ for distances corresponding to the first two maxima and ensuing minima in $g(r)$. For the whole range of r, $n(r)$ decreases monotonically with increase in temperature as a consequence of volume expansion. Thus, at a distance corresponding to the first maximum in $g(r)$, the fractional root-mean-squared fluctuation increases, for increases in T along the orthobaric curve, from 0.44 (or 44%) at $T = 87.9$ K to 0.63 at $T = 140$ K. The value of f(r) when r is equal to the first minimum in $g(r)$, i. e. the radius of the usual first coordination sphere, shows a fluctuation of 13.4% at $T = 87.9$ K, near the triple point, increasing to 21.3% at $T = 140.6$ K, ∼10 K below the critical point. It is found (see below) that fluctuations at larger r are suppressed by the smallness of N and the periodic boundary, particularly at 140.6 K. This is perhaps to be expected because the critical region is characterized by large scale fluctuations in density. The entries in the lower right-hand quadrant of Table 1 probably do not correspond to reality.

Table 1. Calculated fluctuations of radial occupation numbers for distances corresponding to maxima and minima in $g(r)$.

Temp. (K):		87.9	105.5	123.1	140.6
1st maximum	r/Å	3.60	3.70	3.75	3.80
	$n(r)$	3.49	2.73	2.50	2.11
	$f(r)$	0.447	0.527	0.582	0.633
1st minimum	r/Å	5.15	5.35	5.50	5.65
	$n(r)$	13.2	12.1	11.6	10.4
	$f(r)$	0.134	0.163	0.205	0.213
2nd maximum	r/Å	6.85	7.20	7.40	7.50
	$n(r)$	31.9	29.7	28.7	24.6
	$f(r)$	0.083	0.100	0.124	0.129
2nd minimum	r/Å	8.30	8.70	8.95	9.10
	$n(r)$	58.3	53.1	51.2	44.6
	$f(r)$	0.050	0.062	0.082	0.087

Normalized probability distributions about the mean radial occupation function P (n, r) are also obtained and shown for the two extreme temperatures $T = 87.9$ and 140.6 K at $r = 5.5$ Å in Fig. 1.

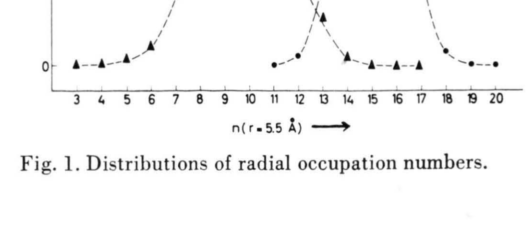

Fig. 1. Distributions of radial occupation numbers.

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[5] W. W. Wood, in: Physics of Simple Liquids, Eds. Temperly, Rowlinson and Rushbrooke, North-Holland, Amsterdam 1968, pp. 114–230.

Numerical values for all four *V-T* points are quoted in Table 2. The curves are approximately symmetric. A notable feature of these distributions is the range; at $T = 87.9$ K there is an 80% probability of finding a radial occupation number n ($r = 5.5$ Å) between 14 and 16 atoms but finite probabilities, are realized during the computations, extend from 11 to 20. With increasing temperature this "tail" effect becomes more pronounced; the range at $T = 140.6$ K is 3 to 17 atoms. These very wide distributions of coordination values are not conformal with those theories of the liquid state based on lattice models [6]. It is, nevertheless, understandable why such models often predict reasonable values for the equation of state. This is simply because the pressure can be expressed as a sum of pair virial functions and the average pressure depends therefore only on the mean radial distribution function.

Table 2. Normalized probabilities of radial occupation numbers at $r=5.5$ Å.

Temp. (K):	87.9	105.5	123.1	140.6
n		$P(n)$		
3				0.0008
4				0.0010
5				0.0069
6			0.0003	0.0221
7		0.0004	0.0025	0.0674
8		0.0015	0.0133	0.1384
9		0.0099	0.0533	0.2102
10		0.0366	0.1438	0.2270
11	0.0005	0.1136	0.2330	0.1802
12	0.0155	0.2479	0.2567	0.0975
13	0.0972	0.2799	0.1860	0.0381
14	0.2245	0.2003	0.0842	0.0090
15	0.3211	0.0863	0.0235	0.0013
16	0.2366	0.0192	0.0030	0.0001
17	0.0892	0.0040	0.0003	
18	0.0143	0.0005		
19	0.0007			
20	0.0001			

The function $w(r)$, obtained at 87.9 K, is shown in Fig. 2. For a perfect gas of non-interacting point particles $w(r)$ is everywhere equal to 1. The curve for liquid argon exhibits a main peak centred at 3.75 Å $\langle$cf. 3.6 for the first peak in $g(r)\rangle$ with a heigh of 0.55. This is followed by a second broad peak at 6.7 Å $\langle$cf. 6.85 for the second peak in $g(r)\rangle$ with an intermediate shallow minimum at 5.85 Å. For this *V-T* point the asymptotic limit of w is reached around $r = 10$ Å and it is evident that the periodic boundary does not restrict fluctuations in radial number density in the region of short-range order. When this result for $w(r \rightarrow \infty)$ is substituted into Eq. (5) to compute the isothermal compressibility, satisfactory agreement is observed with the result obtained by differentiating the computed equation of state for the Lennard-Jones liquid [7]. The predicted value of $w(r \rightarrow \infty)$ is 0.12 and is shown in Fig. 2 for comparison. This is not found to be the case at higher temperatures. For example, when $T = 140.6$ K, and for $r = 10$ Å, fluctuations are around 50% less than might be predicted from the experimental isothermal compressibility. The limiting plateau in $w(r)$ is not observed inside 10 Å for these higher temperatures and the function continues to decrease monotonically after the second peak. This suppression of fluctuations in the range beyond $r \sim 6$ Å by the periodic boundary becomes progressively greater as the temperature increases.

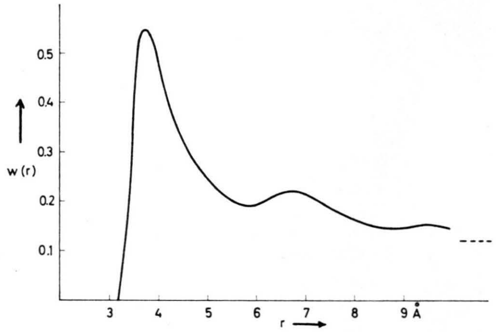

Fig. 2. Local fluctuations of radial number density calculated for a liquid Lennard-Jones system near the triple point. The dashed line corresponds to a limiting value of w as predicted from the isothermal compressibility by Eq. (5).

Conclusions

The functions $f(r)$ and $w(r)$, in addition to $g(r)$, can be obtained in a straightforward manner from MC or MD computations with only a small fraction of additional computational effort. Fluctuations in $n(r)$ are supplementary to $g(r)$ in the description of liquid microstructure. Indeed, without knowledge of $f(r)$ the term coordination number has little or no significance as regards local structure. For sufficiently large N, of the order 10^2 to 10^3 dependent on temperature, the curve $w(r)$ reaches a

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[6] J. A. Barker, Lattice Theories of the Liquid State, Pergamon Press, London 1963.

[7] I. R. McDonald and K. Singer, Discuss. Faraday Soc. **43**, 40 [1969].

limiting value around the same distance as $g(r)$ approaches 1 and this provides a means of computing the isothermal compressibility directly. It is clear that ts the temperature increases along the liquid-vapour coexistence curve a larger sample size N is required. Behaviour of $w(r)$ at large r should serve as a contributory criterion in deciding the optimum value of N in MC and MD computations, particularly when the latter are designed to study liquid structure or to calculate properties which are sensitive to fluctuations in number density.

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