Electron Diffraction and Monte Carlo Studies of Liquids. 2. Transformation of Results to a Common Basis

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Procedures are developed to facilitate the analysis of electron diffraction intensities scattered by liquid clusters, with the ultimate aims of deriving suitable potential functions for intermolecular interactions and of testing current theories of liquids. Treated are the apportionment of electron diffraction intensities from clusters into intermolecular, molecular and atomic contributions, and the effects of truncation of experimental data and of finite sample size in computer simulations that interfere with direct comparisons between experiment and theory.

Dedicated to Professor Otto Bastiansen on his 70th birthday.

In several respects the study of molecular clusters (especially liquid clusters) by electron diffraction is currently at a stage resembling that of the study of gas molecules by electron diffraction when Otto Bastiansen entered the field.[1,*] A number of investigators had already obtained useful structural information, and the fundamental principles of scattering theory had already been formally established. Yet much remained to be optimized in experimental procedures and in practical analyses of diffracted intensity before the full power in the method could be brought to bear. It is widely appreciated that Otto Bastiansen played a giant role in directing the development of the electron diffraction method and bringing it to fruition.[§]

From the standpoint of scattering theory there is no essential difference in interpretation of the diffraction of a beam of electrons by an aggregate of atoms whether the atoms are organized into a molecule or whether they are distributed in a cluster. To the investigator, there is an enormous difference–complexity. With liquid clusters the precise coordinates of each atom are no longer the point of the problem as they were in studies of molecules. What can be learned, and how it can be learned are the themes of this series of papers.

Paper 1[4] dealt with the construction of intermolecular interaction functions to be incorporated into simulations of cluster structure. The aim of the present paper is to describe the development of suitable procedures for comparing results of electron diffraction studies of large liquid clusters with results of Monte Carlo simulations. As pointed out in Paper 1 of this series,[4] it is not possible to extract all the information about clusters that is latent within their diffraction patterns without recourse to theoretical modeling based on statistical thermodynamics. Neither it is possible to carry out modeling adequate for the purpose based upon today's knowledge of molecular interactions. It *is* entirely feasible, however, to refine experimental and theoretical analyses together in such a way that each benefits from the other. Nevertheless, there arise problems associated with the incompleteness in the experimental data and with limitations in the size of systems treated in Monte Carlo simulations. These problems would remain even if it were assumed that

*See, for example, Ref. 2.

§It is also of interest that Bastiansen's early diffraction research (Ref. 3) was directed toward the study of liquids, the principal object of the present series of papers.

the laws of molecular interactions are fully established and that the diffraction intensities are free of detectable error.

In the following analyses we shall address some of the more important problems without attempting to account for all potential sources of trouble. For example, it will be assumed that the clusters are sufficiently large that their pair correlation functions correspond to those of the bulk – even though a not inappreciable fraction of the molecules are in the surface layer. First will be considered effects of incompleteness in range of scattering angle in diffraction patterns and in range of pair correlation functions in Monte Carlo simulations.

Effects of truncation

A. *Available range of diffraction data.* Before analyzing problems associated with the finite range of data available from experiment and theory it may be helpful to consider some general aspects of resolving power. Irrespective of whether the internal structure of an object is determined by microscopy, holography, or diffraction, the principles are substantially the same. To resolve fine detail a combination of small wavelength (λ) and large numerical aperture ($\sin\theta_m$ *in vacuo*) is needed. According to the usual definition of resolving power, the smallest separation, Δr, that can be resolved is[5]

$$\Delta r \approx 0.6\,\lambda/\sin\theta_m \qquad (1)$$

where θ_m is the angular displacement from the optic axis of the outermost rays diverging from the object and entering the objective lens (or registering upon the hologram or diffraction pattern). In diffraction theory, intensities are customarily expressed as a function of the natural scattering variable s whose magnitude is given by:

$$s = (4\pi/\lambda)\,\sin\theta/2. \qquad (2)$$

The limit of resolution in diffraction experiments, then, is

$$\Delta r \approx 4/s_{max}, \qquad (3)$$

according to which atomic separations are readily resolved if s_{max} is of the order of 10 Å^{-1}, a common value in cluster studies (cf. $s_{max} \approx 30$ to 60 Å^{-1} in gas-phase determinations of molecular structure). Eqn. (3) also shows, however, that scattering at small angles inside, say, $s = 0.8$ Å^{-1} is not sensitive to fine detail in the distribution of scattering sites. We shall make use of this fact in a later section.

The small-angle insensitivity to structure is fortunate because intensities of the *elastically* scattered electrons needed for structure analyses are difficult to measure with high precision at small scattering angles. Below $s = 1$ Å^{-1}, scattered intensity begins to be dominated by inelastic scattering. For this reason, measurements in our laboratory are recorded only into about 0.8 Å^{-1}. On the other hand, there is no particular difficulty in following elastically scattered diffraction features out to the largest angles to which interference effects extend. By contrast, in X-ray diffraction experiments inelastic scattering is negligible at very small angles but begins to dominate at intermediate to large angles.

Because of truncation of data at small angles, together with problems arising from the form of atomic scattering factors at small angles,[6] it is not entirely straightforward to derive the pair correlation functions of molecular liquids by Fourier transformation of electron diffraction intensities. The identical problem occurring in gas-phase electron diffraction investigations of molecular structure presents no obstacle to the derivation of structures with considerable precision. Structures are almost universally determined in refinements of intensities, not radial distribution functions. For the same reasons it is preferable to judge the validity of a simulation of cluster structure by its success in reproducing the diffracted intensity profile.

The foregoing conclusions concerning resolving power can be derived from the theoretical expression for the cluster structure function $sH_d(s)$, which we shall need also for other purposes. By definition:

$$sH_d(s) \equiv sI_{cl}(s)/I_{at}^{el}(s) \qquad (4)$$

where $I_{cl}(s)$ is the net interference intensity from the *intermolecular* internuclear distances and $I_{at}^{el}(s)$ is the elastically scattered component of the atomic intensity. The structure function can, in turn, be written as the sum

$$sH_d(s) = \sum_i \sum_{<j} sH_{ij}(s) \quad (5)$$

over contributions from various types of atom pairs (e.g., in benzene, C···C, C···H and H···H). According to the usual (semi-kinematic) scattering theory adopted,[6] these components are given by Eqn. (6), where the coefficients C_{ij}^d are the

$$sH_{ij}(s) = C_{ij}^d \mu_{ij}^d(s) \int_0^{r(\max)} 4\pi r \bar{\varrho}_{ij} g_{ij}(r) \sin sr dr \quad (6)$$

constants $Z_iZ_j/\Sigma_k Z_k^2$ approximately representing the effective electron scattering powers (nearly proportional to products of atomic numbers), while the functions

$$\mu_{ij}^d(s) = \frac{|f_i| \cdot |f_j| \cos\Delta\eta_{ij}}{Z_iZ_j} \cdot \frac{\Sigma_k \Sigma_k^2}{\Sigma_h |f_k|^2} \quad (7)$$

modify the C_{ij} to account for the exact form of the electron scattering factors $f_k \exp(i\eta_k)$. The modification functions $\mu_{ij}^d(s)$ deviate only slightly from unity except at small angles of scattering. Coefficients $\bar{\varrho}_{ij}$ are the mean numbers of atom pairs i,j per unit volume.

It can be seen from Eqn. (6) that the pair correlation functions $g_{ij}(r)$ could be derived from a Fourier sine transform of the experimental structure function if the coefficients $\mu_{ij}(s)$ were truly constant (which they are, if all the atoms are of the same kind). Even when the $\mu_{ij}(s)$ are not constant, Fourier transforms of the experimental data can sometimes be helpful in evaluating the performance of simulations of liquid structure.*

B. *Available range of data from simulations.* An important inference that can be made from diffracted intensities is the distance over which correlations in molecular positions persist in liquids. The larger the range, the sharper the initial intensity maximum in the diffraction pattern. Unfortunately, it is impractical to try to simulate this feature faithfully in Monte Carlo or molecular dynamics simulations of supercooled liquids. This is because such simulations are so demanding computationally that runs must be severely restricted in sample size. For example, our Monte Carlo computations on benzene molecules incorporating twelve interaction sites per molecule are based on 128 molecules in a cubic region $L \times L \times L$, with periodic boundary conditions. While this sample size is equivalent computationally to one with more than 1500 Lennard-Jones spheres, it cannot be relied upon to yield trustworthy pair correlation functions beyond $L/2$ or so, or about 13 Å. This is a substantially shorter distance than that over which correlations are observed to survive in cold clusters. Therefore, any potentially sharp features in diffraction patterns are badly washed out in simulations because of the severe truncation characteristic of the Monte Carlo calculations.

The magnitude of the washing out is easily estimated. As shown in Eqn. (6), $sH_{ij}/\mu_{ij}^d(s)$ is the Fourier sine transform of $rg_{ij}(r)$. Hence, what is true about resolution in r-space when $sH(s)$ is truncated at s_{max} must also be true in s-space when $g(r)$ is truncated at r_{max}. The limit of resolution of detail in the structure function $sH(s)$ – or, what amounts to the same thing, the blurring of features in $sH(s)$ – can be inferred from Eqn. (3) to be

$$\Delta s \approx 4/r_{max}. \quad (3b)$$

Since r_{max} is of the order of 10–20 Å in Monte Carlo simulations, features as narrow as ~0.5 $Å^{-1}$ will not be reproduced faithfully. Special attention must be given to procedures to enable definitive comparisons to be made between theory and experiment.

A modest extension beyond $L/2$ has been resorted to in an attempt to lessen slightly the truncation problem. The rationalization is as follows. For molecules in a cubic box with periodic boundary conditions, site-to-site distances greater than $L/2$ in any direction perpendicular to a box wall correspond to site-to-site distances less than $L/2$ in the opposite direction. Correlations beyond (or even close to) $L/2$ in these directions must be spurious to a large degree in a noncrystalline phase. Correlations along the diagonals may be somewhat freer of effects of the boundary conditions. Therefore, histograms were accumulated beyond $L/2$ in directions pointing away from normals to the box walls. Details are given in the Appendix.

*See, for example, Ref. 7.

C. *Dealing with truncation problems.* As we have seen, truncations of experimental and theoretical data are of such a nature as to interfere with a *direct* comparison of experimental and theoretical results. The simplest way to handle the difficulty is to transform both the theoretical and experimental results until they correspond to the same basis. Calculated pair correlation functions, then, are transformed into calculated structure functions $sH_d(s,D)$ for spherical clusters of diameter D restricted to be only somewhat greater than $L/2$. Next, experimental structure functions are modified to correspond to structure functions of smaller spherical clusters, also of diameter D, characterized by the same internal cluster structure. Both steps in this strategy can be accomplished objectively, as follows.

D. *Dependence of simulated structure function on cluster diameter.* First, consider the point-to-point pair correlation function $\alpha(r,D)$ corresponding to sites uniformly distributed in a sphere of diameter D. This function is given by[8]

$$\alpha(r,D) = 1 - 3(r,D)/2 + (r/D)^3/2, \; r<D$$
$$= 0, \; r>D. \qquad (8)$$

If it is assumed that the pair correlation function $g_{ij}(r,D)$ in a spherical cluster of diameter D matches that of a bulk phase described by $g_{ij}(r)$ as closely as possible, then

$$g_{ij}(r,D) = \alpha(r,D)g_{ij}(r). \qquad (9)$$

When this modified pair correlation function is introduced into Eqn. (6) with r_{max} now equal to D, the (numerically integrated) result, completed via Eqn. (5), can be compared with the observed structure function of a cluster after the modification described in the next section.

E. *Modification of observed structure function.* As in the previous section, the object is to transform a structure function corresponding to a large cluster [with pair correlation functions $g_{ij}(r)$] to that of a small cluster [with pair correlation functions $g_{ij}(r,D)$, cf. Eqn. (9)]. To effectuate this directly from the experimental structure function when the functions $g_{ij}(r)$ are unknown, the Fourier folding theorem[9] can be invoked. According to this theorem, if $sH_{ij}(s)$ corresponds to $g_{ij}(r)$ via Eqn. (6) for a cluster large compared with D, then $sH_{ij}(s,D)$ can be written as Eqn.

$$sH_{ij}(s,D) = (2\pi)^{-1/2}\int_{-\infty}^{\infty} s'H_{ij}(s')\dot{t}(s-s')ds' \qquad (10)$$

(10), where the modification function $t(s)$ is the Fourier cosine transform of $\alpha(r,D)$, or as given

$$t(s) = (2/\pi)^{1/2}\int_0^{\infty} \alpha(r,D)\cos sr dr \qquad (11)$$
$$= (2\pi)^{-1/2}(3D/w^4)\{w^2 - 2w\sin w + 2(1-\cos w)\}$$

by Eqn. (11), where w is sD. Since $t(s)$ is nearly Gaussian in the upper 95 % of its profile, it introduces little error to simplify to

$$t(s) = 3D(32\pi)^{-1/2}\exp(-s^2/2\sigma_s^2) \qquad (12)$$

with $\sigma_s \approx 3.34/D$ and to reduce the limits of integration in Eqn. (10) to $\pm 4\sigma_s$ or less.

A practical problem arises when applying the above procedure to experimental data. The blurring out of features in the intensity curve by means of a numerical integration approximating Eqn. (10) corresponds to superposing a series of representations of the diffraction pattern displaced from each other. Obviously, this introduces errors in the vicinity of points at which $sH_d(s)$ has been truncated. Intensities within about $3\sigma_s$ (about 0.5 $Å^{-1}$ for benzene) of the truncation point are appreciably distorted. This is serious because the sharpest small angle feature characteristically lies within about 0.5 $Å^{-1}$ of the low-angle cut-off of measurements. This source of trouble can be handled quite reasonably, however. The loss of data can be mitigated by grafting theoretical data inside the small-angle cut-off. Since the small-angle intensities are much less sensitive to structural detail than are intensities further out (cf. section A, above), the theoretical model need not be perfect to work reasonably well. Intensities calculated from RISM simulations[7] can be (and have been) used. An even simpler model may suffice, however, and it also serves another useful role that will be discussed later. This model is described in the next section.

Step function model

To a rough approximation, pair correlation functions $g_{ij}(r)$ are step functions, zero inside the dis-

tances of closest atomic contact and unity, on average, beyond this distance. Let us denote the step function as $g^{o}_{ij}(r)$, where

$$g^{0}_{ij}(r) = 0, \ 0 < r < r_0 \tag{13a}$$

$$= 1, \ r_0 \leq r < \infty \tag{13b}$$

and introduce the corresponding function

$$g^{0}_{ij}(r,D) = \alpha(r,D)g^{0}_{ij}(r) \tag{14}$$

for step-function clusters of diameter D. The associated function $sH^{o}_{ij}(s,D)$ is, from Eqn. (6),

$$sH^{0}_{ij}(s) = C^{cl}_{ij}\,\mu^{d}_{ij}(s)(4\pi\bar{\varrho}_{ij}/s^2)(\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4) \tag{15}$$

where, letting $u \equiv sD$ and $v \equiv sr_o$,

$$\vartheta_1 = (3/u - 12/u^3)\cos u, \tag{16}$$

$$\vartheta_2 = -(12/u^2)\sin u, \tag{17}$$

$$\vartheta_3 = (v - 3v^2/2u + 3/u + v^4/2u^3 - 6v^2/u^3 + 12/u^3)\cos v, \tag{18}$$

and

$$\vartheta_4 = -(1 - 3v/u + 2v^3/u^3 - 12v/u^3)\sin v. \tag{19}$$

The much simpler function $sH^{o}_{ij}(s)$ for bulk liquid results in the limit of very large u.

Although it scarcely affects the small-angle behavior of $sH^{o}(s)$, it is worthwhile to present the result of softening the harsh step function. If it is assumed that the atomic contact is not distributed about r_o as a delta function but, rather, according to

$$P(x) = (2\pi\sigma_r^2)^{-1/2}\exp(-x^2/2\sigma_r^2) \tag{20}$$

where $x = r'_o - r_o$ and r'_o is the variable contact pertaining to soft atoms in thermal motion, it can be shown that the smoothed pair correlation function is

$$g^{s}_{ij}(r) = [erf(Z)]/2 \tag{21}$$

where Z is $(r-r_o)/(2\sigma_r^2)^{1/2}$. The effect of this smoothing upon the structure functions is given by

$$sH^{s}_{ij}(s,D) = sH^{0}_{ij}(s,D)\exp(-\sigma_r^2 s^2/2) \tag{22}$$

where it is to be understood that r_o and σ_r each depend upon the atom pair i,j and the temperature involved. One way to estimate plausible values of r_o and σ_r for comparison with Monte Carlo simulations is to identify r_o with the value of r at which $g_{ij}(r)$ first becomes 0.5, and to deduce σ_r from the slope of $g_{ij}(r)$ at r_o via

$$[dg^{s}_{ij}(r)/dr]_{r_0} = \{d[erf(Z)]/2dr\}_{r_0} = (2\pi\sigma_r^2)^{-1/2}. \tag{23}$$

A comparison of structure functions for benzene at 160 K derived from a Monte Carlo simulation[10] and from eqns. 15–23 with D = 18 Å is shown in Fig. 1. It is evident that the gross features of $sH_d(s)$ [or $sM_{cl}(s)$] are governed by the step functions $g^{o}_{ij}(s)$ but that the shapes of the features are strongly influenced by details of the molecular interactions.

Apportionment of diffracted intensities

To a good approximation (the independent atom model) the total intensity of electrons diffracted by clusters can be written as the sum

$$I_{tot} = I^{el}_{at} + I^{inel}_{at} + I_{mol} + I_{cl} + I_{cg} \tag{24}$$

where the first two components are the elastic and electronically inelastic contributions scattered by the atoms, I_{mol} represents the intramolecular interference terms and I_{cl}, the "cluster" intermolecular interference terms associated with internuclear distances between different molecules in the cluster. The last contribution, I_{cg}, refers to intensity scattered by the carrier gas. In the following discussion we shall assume that I_{cg} has already been subtracted as described elsewhere.[11] Because of the (Rutherford) mechanism of electron scattering, $I_{tot}(s)$ is an extremely rapidly falling function of s but one that is readily amenable to visual inspection or numerical analysis if "leveled" by division by the theoretical atomic scattering to obtain $I^{tot}_{o}(s)$, or

$$I^{tot}_{0}(s) = I_{tot}(s)/(I^{el}_{at} + I^{inel}_{at})_{theor} \tag{25}$$

where the atomic intensity is that of the *clusters*,

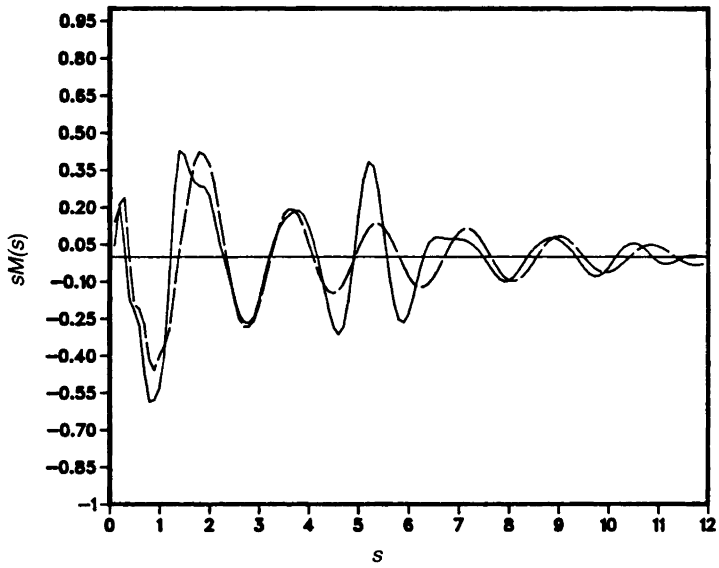

Fig. 1. Structure function $sM_{cl}(s)$ for 18 Å benzene clusters at 160 K. Solid curve: Monte Carlo calculation with potential function of Ref. 10. Dashed curve: step-function model.

the contribution by carrier atoms being purposefully left out.

A difficulty with this procedure in ordinary molecular structure analyses that is compounded in cluster studies, is that systematic errors in experiment and (even more) in theory make it inadequate merely to level the intensities with the theoretical atomic intensity I_{at}^{th}. Even though large-angle electron scattering is dominated by nuclear scattering, in the small-angle range of interest in cluster research, electron diffraction intensities are far more sensitive to electron correlation and redistribution of charge in covalent bonding than are X-ray intensities. Therefore, to compensate for systematic errors, a suitable reduced intensity denoted $M(s)$ is found by passing a smooth polynomial background $B(s)$ through the theoretically leveled intensities, and by division, once more, by this smooth background to obtain $M(s)$. In standard molecular structure refinements (where I_{cl} and I_{cg} are zero), then

$$R \cdot M_{mol}(s) = [I_0(s)/B(s)] - 1 \qquad (26)$$

where R, the "index of resolution", is an empirical constant close to unity, introduced to compensate for systematic experimental and theoretical errors. The objective criterion for establishing R and the polynomial coefficients of $B(s)$ is to refine them simultaneously with the molecular structure parameters, entering $I_{mol}^{th}(s)$ until the difference between calculated and experimental $M(s)$ functions is minimized. Experience demonstrates that this procedure leads to excellent results.

An analogous procedure for liquid clusters would require a coupling of potential parameters in Monte Carlo refinements with background coefficients in diffraction experiments – an impracticable approach. In early cluster studies, reasonably good backgrounds were established by entering the known molecular structure parameters into I_{mol} of Eqn. (24) and passing a smooth polynomial background through I_{tot}/I_{at}^{th} in such a way as to minimize residuals, ignoring any effect of I_{cl}. This procedure led to quite good structure functions I_{cl}/I_{at} in the intermediate to large angle scattering. It was not entirely satisfactory in the small angle region, where theoretical uncertainties are most severe and where there was no objective criterion to establish the background. Fortunately, this region is the region of least sensitivity to cluster structure, as explained in previous sections. Therefore, the step-function representation of the preceding section establishes the main features of I_{cl}, except for

a high frequency ripple that is important in structure inferences but relatively harmless in constructing the smooth background B. Accordingly, theoretical expressions are available for the reduced functions $M_{mol}^{th}(s)$ and $M_{cl}^{th}(s)$, so that from Eqn. (6) can be written

$$I_0^{tot}/B - R \cdot M_{mol}^{th} - M_{cl}^{th}$$
$$= [(I_{at}^{el} + I_{at}^{inel})/I_{at}^{th}]/B. \quad (27)$$

The result of these subtractions is a fairly smooth "atomic curve" that is to be cleaved by the smooth background function B in such a way as to leave minimum residuals. Once B is established by least-squares, the reduced intensity is given by

$$M_{cl}(s) = (I_0/B) - R \cdot M_{mol}(s) - 1. \quad (28)$$

In the most careful work, $M_{mol}(s)$ is obtained experimentally from the unclustered molecules to correct for the (usually very small) systematic errors in $M_{mol}^{th}(s)$.[12] Finally, it is advantageous to convert to the cluster structure function of more universal interest

$$sH_d(s) = sM_{cl}(s) \times (I_{at}^{el} + I_{at}^{inel})^{th}/(I_{at}^{el})^{th} \quad (29)$$

with the aid of the theoretical atomic intensities. Here, systematic errors in theoretical atomic intensities have a much smaller effect than in establishing the original atomic background intensity.

Concluding remarks

Now that electron diffraction experiments on cold liquid clusters are beginning to generate data of high quality, it is important to analyze the results carefully to extract realistic information about molecular interactions and assess the validity of conventional treatments of molecular liquids. Because of fundamental limitations in current experimental and theoretical techniques, there are problems in comparing experiment and theory directly on the same basis. The most important difficulties have been analyzed in the foregoing sections, and procedures to overcome them have been developed. In the next paper of this series[10] these procedures will be implemented in a comparison of results of experimental and Monte Carlo studies of benzene.

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Appendix

Computation of pair correlation functions. In a Monte Carlo run with N_m molecules in a box $L \times L \times L$, the coordinates of all interaction sites are saved periodically, for a total of N_s saved outputs. A sub-routine uses the site coordinates to construct the atomic coordinates (which may differ from the interaction site coordinates) for the purpose of calculating the pair correlation functions $g_{ij}(r)$ and electron scattered intensities. Each molecule has n_i atoms of kind i and n_j atoms of kind j (i and j may be the same kind). All intermolecular internuclear distances r_{ij} in the sample of N_m molecules are calculated starting with reference atom i and locating for each atom j not in the reference molecule the "nearest image" of atom j (which may be in an adjacent box if i is not close to the box center). Histograms of each pair type (e.g. CC, CH, HH in a hydrocarbon) are accumulated, with $N_{ij}(r_k)$ outcomes accepted from $r_k - \Delta r/2$ to $r_k + \Delta r/2$. If r_k is less than $L/2$, no part of the surface of a sphere of radius r_k centered on atom i lies outside the region of sampled atoms j. For $L/2 < r_k < L/2^{1/2}$, the sampled atoms j populate, on average, only the fraction $(3L/2r_k) - 2$ of the surface of the sphere of radius rk. No sampled atoms lie beyond $3^{1/2}L/2$, and those lying beyond $L/2$ tend to be concentrated along directions parallel to the box diagonals.

The average number of atoms j, namely dN_{ij}, lying at a distance from reference atom i between r and $r + dr$, is by definition $4\pi r^2 \bar{\varrho}_{ij} g_{ij}(r)dr$, where $\bar{\varrho}_{ij}$ is the mean density $n_j N_m/L^3$. From the accumulated histograms $N_{ij}(r_i)$, then, the pair correlation function $g_{ij}(r_k)$ can be calculated, including all atoms n_i in the reference molecule and all N_m molecules, from

$$g_{ij}(r_k) = N_{ij}(r_k)L^3/(2\pi r_k^2 K n_i n_j N_m^2 N_s \Delta r) \quad (A1)$$

for $r_k < L/2$, where K is unity if i and j are of the same kind, or 2 otherwise. As mentioned in the

text, spurious correlations are not quite as severe along diagonals of the box as along directions perpendicular to the box faces. Therefore, it is plausible to extend the calculation of $g_{ij}(r)$ somewhat beyond $L/2$ by inserting the corresponding histograms $N_{ij}(r_k)$ into the expression (A1) and dividing by the fraction $(3L/2r_k) - 2$ noted earlier, to normalize in the region $L/2 < r_k < L/2^{1/2}$. Pair correlation functions so calculated in this extended region have so far looked reasonable. Inasmuch as the only use made of them is in the calculation of ${}^{g}{}_{ij}(r,D)$ curves for small clusters and the corresponding intensities [cf. eqns. (9) and (10) with $D \leq L/2^{1/2}$], in which the weighting function $\alpha(r,D)$ of eqn. (8) assigns very low weights to the region $L/2 < r < L/2^{1/2}$, there seems to be some adantage and little risk in extending data into this equivocal region of r.

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