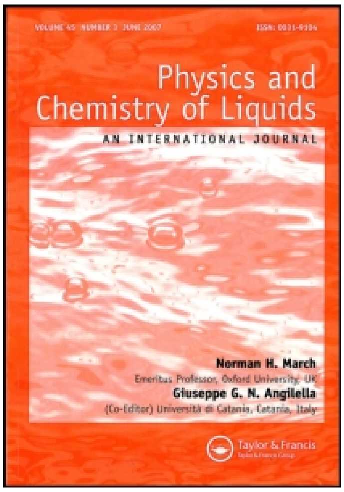

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SPATIAL TRANSITIONS BETWEEN LOCAL STRUCTURES IN CONDENSED SYSTEMS

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Scattering data and radial distributions in amorphous matter can be represented accurately in terms of models based on a small set of structural elements which specify local atomic configurations, and on certain spatial random processes specifying the fraction of such elements and the decay of their correlations with distance. The local structural elements, expressed in terms of globally ordered structures, particularly in terms of lattices (L), are subject to radially evolving Markoffian-like processes of relative displacements and of transitions between Ls at different points in space. Including an empty lattice L_0 in the set (L) leads to a definition of random voids and their spatial correlations, depending on the size of the local domains considered. The models provide representation of a continuous range of amorphous structures from liquids and glasses via nanomaterials to crystalline powders.

Keywords: Markov processes; Paracrystals; Free volume

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1. INTRODUCTION

Classical theories of liquids consider as their major goal to provide workable functional relations between intermolecular potentials and molecular distributions. The standard assumption is that one can express the latter with reasonable accuracy by effective pair potentials. Yet, limitations on a full implementation of such a program lead naturally to search for different characteristics parameters related to both structure and interaction. In particular, the use of local lattice models [1–4] in conjunction with *spatial* random processes [5–9] provides an efficient tool for accurate and consistent [10] analytic representations of empirical structure functions of condensed disordered systems. By defining parent ordered structures (L) and specifying the random processes by a small number of parameters (D), this approach provides a small set of parameters (L, D) which completely determine all structural properties of the system and gives a compact view of local atomic positions. Moreover, since the parameter values span a low-dimensional "structure space" whose points represent real or virtual states of the system, this can be used to advantage in following both macroscopic and

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microscopic changes along paths in the (L, D) space. For example, given molecular interactions, one can devise an extrapolation procedure of the energy of a disordered structure to the energy of an ordered lattice structure L, enabling accurate evaluation of corresponding lattice sums [11]. Furthermore, one can evaluate the entropy of a disordered system [12] utilizing the Third Law, by following the entropy change along a path from the disordered state (L, D) to the ordered state $(L) \equiv (L,\ D=0)$. Thus, all thermodynamic properties of the system can be evaluated from structure data and given molecular interactions. Of a central role in such calculations is the radial distribution represented as a function of the parameter set, $g(\mathbf{r}) = g(\mathbf{r};\ L,\ D)$. It can be utilized in any method which reduces contribution of higher order correlations and many-body interactions to functionals of the pair correlations. Indeed, in evaluation of the entropy from structure data [12], such a method was required to evaluate spatial energy fluctuations. Another example is the embedded atom method [13,14] where the electron density at an atomic site due to all other atoms is approximated by a superposition of electron densities.

The random processes considered here are intended to produce radial pair distributions, hence are restricted to radially evolving Markoffian-like processes. Higher order distributions can be derived from extensions of the Markoffian-like process to mullti-theta (multi-Gaussian-like) distribution [15]. In previous applications the only spatial random process employed was structural diffusion (SD) and modifications thereof (see below). Yet, with hardly additional effort the model can be extended to include also processes of structural transition (ST) between several local substructures [4] L_α, $L_\beta, \ldots$ Such an extension, briefly sketched in [7], provides a reformulation of frequently applied modeling of pairs distributions as resulting from a mixture of two different local lattice structures (see e.g., references in [4]) in terms of spatial random processes. It enables significant refinements leading to an accurate representation of the scattering function $S(\mathbf{k})$ over the entire $\mathbf{k}$ range, and relate the global spatial density fluctuations, exhibited by nonzero $S(0)$, to the structure parameters $(L,\ D)$.

In the following we consider an extension including, beside a local lattice structure L_1, an "empty lattice" L_0. With the random spatial processes involved this scheme leads to a workable definition of a random excess volume, considered a characteristic feature of amorphous structures. An excess volume has been dealt with by various statistical theories, considering such entities as holes [16], cavities [17–20] (voids) in liquids, free volume [21], or voids between atoms in glasses [22], distributed randomly in space. Several such theories are based on assuming an underlying reference lattice [23] serving to count different atomic configurations. However, the present approach offers a procedure for extracting information on random excess volume directly from structure data. Necessarily it depends on our choice of the underlying local lattice L_1, which reflects limitation on our ability to discern a global pattern in an ensemble of local atomic configurations [12,24].

In Section 2 we outline the SD model. Section 3 deals with its ST extension and consequent partial radial distributions. Section 4 specializes the foregoing results to a system with random excess volume and leads to an analytic expression for its radial distribution $g(\mathrm{r})$. In Section 5 we present the corresponding expression for the static scattering function, $S(\mathbf{k})$, and consider the consequences of its analytic properties. In Section 6 we consider several limit points of the model "structure space", including the "ideal glass", nanomaterials, crystalline powder, and separate bulk phases. General consequences of the program implied by the SDT models are summarized in Section 7.

2. RANDOM DISPLACEMENT OF A LOCAL LATTICE

The model used, which was termed, following Frenkel [5], SD model, relates local atomic configurations to a (virtual) lattice L, subject to random displacements, $\mathbf{s}=\mathbf{s(r)}$, in space. The local density, which for a given configuration of N particles, $\mathrm{r}^N \equiv (\mathrm{r}_1, \mathrm{r}_2, \ldots, \mathrm{r}_N)$, is given by

$$\rho(\mathbf{r}) \equiv \rho(\mathbf{r}; \mathbf{r}^N) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i), \tag{1}$$

is now approximated by

$$\rho(\mathbf{r}) = \rho(\mathbf{r}; \mathbf{s}) = \sum_{\mu, \sigma} \delta(\mathbf{r} - \mathbf{a}_\mu - \mathbf{a}_\sigma - \mathbf{s}), \tag{2}$$

where the double sum runs over all lattice points of L; the μ-sum counts the position vectors $\mathbf{a}_\mu$ of the unit cells of L, and $\sigma = 1, \ldots, n$, counts the points $\mathbf{a}_\sigma$ inside one unit cell. The average local density is

$$\rho = \langle \rho(\mathbf{r}; \mathbf{s}) \rangle = \frac{1}{v} \int_v \rho(\mathbf{r}; \mathbf{s}) d^3\mathbf{s} = \frac{n}{v}, \tag{3}$$

where v is the volume of the unit cell of L. The random process $\mathbf{s}(\mathbf{r})$ is chosen to be a radially evolving diffusion in the space of displacements $\{\mathbf{s}\}$ modulo in the unit cell of L. Thus, given a pair of points in space, $\mathbf{r}_1$, $\mathbf{r}_2$, and the respective random displacements, $\mathbf{s}_1$, $\mathbf{s}_2$, the conditional probability density function, $\mathbf{P}(\mathbf{s}|r)$, for a relative displacement $\mathbf{s} = \mathbf{s}_1 - \mathbf{s}_2$, $(\mathrm{r} = |\mathrm{r}_1 - \mathrm{r}_2|)$, is assumed to obey for large r a diffusion type equation,

$$\frac{\partial \mathbf{P}}{\partial r} = D \nabla_{\mathbf{s}}^2 \mathbf{P}, \tag{4}$$

where D is a "structural diffusion" coefficient. Equation (4) is to be understood as applying to large r, where the Markoffian assumption is valid. To allow for deviation from a strictly Markoffian process for small r, we replace D by $W'(r)$, where $W = W(r)$ has the asymptotic forms

$$W \sim Dr, \quad r \to \infty; \qquad W'(r) \to 0, \quad r \to 0. \tag{5}$$

The solution of (4), periodic in $\mathbf{s}$, is given by

$$\mathbf{P}(\mathbf{s}|r) = \frac{1}{v} \sum_{\nu} e^{-W \mathbf{b}_\nu^2} e^{i \mathbf{b}_\nu \cdot \mathbf{s}}. \tag{6}$$

Here the ν-sum extends over all points, $\mathbf{b}_\nu$, of the reciprocal lattice L^*. Clearly, (6) satisfies the boundary condition

$$\mathbf{P}(\mathbf{s}|\mathbf{r}) = \delta(\mathbf{s}), \quad \text{when } W = 0. \tag{7}$$

Now (6) can be applied directly to evaluate the average

$$G(\mathbf{r}) = \langle \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\rangle/\rho = \rho g(\mathbf{r}), \quad r \neq 0, \tag{8}$$

where $G(\mathrm{r}) = G(\mathrm{r},\ t = 0)$ is the van Hove correlation function [25] at $t = 0$, and $g(\mathrm{r})$ is the radial distribution. Since $G(\mathrm{r})$ includes also the self-correlations of particle densities, the second equality in (8) holds strictly only for $\mathbf{r} \neq 0$. Evaluating (8), we obtain

$$G(\mathbf{r})/\rho = g(\mathbf{r}) = g(\mathbf{r};\ L, D) = \sum_{\nu} \mathrm{C}_{\nu} e^{-\mathrm{W}b_{\nu}^{2}} \langle e^{W\mathbf{b}_{\nu}\cdot\mathbf{r}}\rangle_0, \qquad C_{\nu} = \left| \frac{1}{n} \sum_{\sigma} e^{i\mathbf{b}_{\nu}\cdot\mathbf{a}_{\sigma}} \right|^2, \tag{9}$$

or alternatively, applying the Poisson sum transformation formula,

$$G(\mathbf{r}) = \rho g(\mathbf{r};\ L, D) = \sum_{\mu} \frac{1}{n} \sum_{\sigma,\sigma'=1}^{n} \frac{1}{(4\pi W)^{3/2}} \left\langle \exp\left[\frac{(\mathbf{r} - \mathbf{a}_{\mu} - \mathbf{a}_{\sigma} + \mathbf{a}_{\sigma'})^2}{4W} \right] \right\rangle_0. \tag{9a}$$

The brackets $\langle\rangle_0$ denote averaging over all orientations of L, or of r. By (9), $g(\mathrm{r})$ is an analytic function (a theta-type series), depending on the parameter set (L, D). Clearly, the series (9) is fast converging for large r (large W) whereas (9a) is fast converging for small $\mathbf{r}$. In (9a) $G(\mathrm{r})$ is expressed as a sum of quasi-Guassian distributions centered around the lattice points of L at positions $\mathbf{a}_{\mu} + \mathbf{a}_{\sigma}$ relative to points $\mathbf{a}_{\sigma'}$ inside one unit cell, and averaged over all orientations of $\mathbf{r}$ (or L).

Expressions similar to (9a) (but not identical to it) have been repeatedly used [1,5,9] to reproduce $g(\mathrm{r})$ data. Expressions similar to (9) are used as well [2,3], mainly to obtain good fits to scattering data in the low k range. However, presently we obtain two equivalent representations of $g(\mathbf{r})$ following general notions of random spatial processes specialized to a radially evolving diffusion-like process, specified by a dispersion (width function) $W(r)$. For the numerical evaluation of $g(\mathbf{r})$, the following specialization of $W(r)$ can be made: Because of exclusion effects, we expect $g(\mathrm{r}) = 0$ to hold to a good approximation within an entire domain $0 \leq r \leq r_0$, where r_0 is of the order of nearest neighbor distance. This is achieved by choosing for $W(r)$ a function which goes fast to zero for $r \leq r_0$. For practical reasons of analytic manipulation and of numerical convergence at small r we choose for W the particular form

$$W = W_0 + Dr_0\omega\left(\frac{r}{r_0}\right), \qquad W_0/r_0^2 \ll D/r_0 \ll 1 \tag{10}$$

where

$$\omega(x) = \omega_1(x) = \log\cosh x. \tag{11.1}$$

Another form used for $\omega(x)$ was [8]

$$\omega(x) = \omega_2(x) = \sqrt{1 + x^2} - 1. \tag{11.2}$$

Both choices have the asymptotic form

$$\omega(x) = \frac{1}{2}x^2 + O(x^4), \quad x \to 0,$$

but for $x \to \infty$

$$\omega_1(x) = x - \log 2 + O(e^{-2x}), \qquad \omega_2(x) = x - 1 + O\left(\frac{1}{x}\right). \tag{11i}$$

Both forms of $\omega(x)$ have the advantage over an earlier choice [26] in that the requirement of a positive scattering function [27,28], $S(\mathbf{k}) > 0$, is satisfied for all $\mathbf{k}$, but (11.1) has been found preferable since it produces a better fit to $g(\mathbf{r})$ of the steep rise at the small r side of the first peak. A plot of the two width functions, with the same asymptote, are shown in Fig. 1. By (11i), for large r one has $W(r) \approx D(r - r_c)$, where $r_c = r_0 \log 2$ or $r_c = r_0$ for (11.1) or (11.2), respectively. When we put $r_0 = 0$ in (10), we retrieve the simple law $W = Dr$.

A further generalization of (10), used in the following, is to replace the nonconstant term by a sum of two or more terms, i.e.

$$W = W_0 + \sum_i D_i r_i \omega\left(\frac{r}{r_i}\right), \quad r_1 < r_2 < \cdots \tag{10'}$$

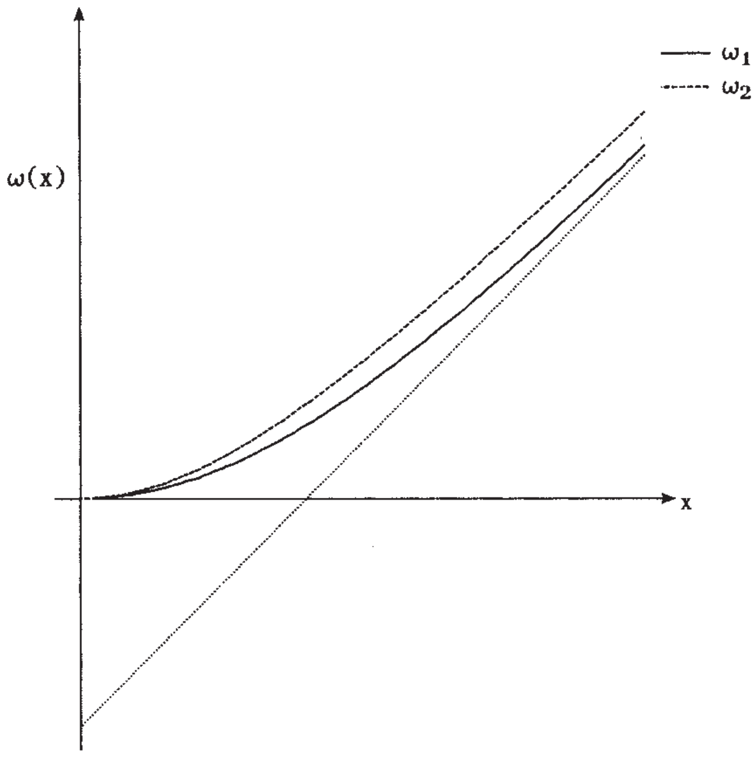

FIGURE 1 Radially evolving width functions (Eq. (11)) with a common asymptote.

(See also [29].) By (11i), for $\mathbf{r} \sim r_1$ or smaller the $i = 1$ term dominates whereas for large $\mathbf{r}$, applying (11.1),

$$W \sim W_0 + \sum_i D_i(r - r_{ci}), \quad r_{ci} = r_i \log 2.$$

3. SPATIAL RANDOM TRANSITIONS BETWEEN LOCAL STRUCTURES

The accuracy of reproducing $g(\mathbf{r})$ with the model representation (9) depends on the degree of complexity of L, i.e. on the size of n. Clearly, by increasing n to a "macroscopic" value, say of the order of 10^3, the points in the unit cell of L become a representative configuration in a typical computer simulation of a macroscopic system, in particular in the reverse Monte Carlo procedure for reproducing empirical $g(\mathbf{r})$ data [30]. With the parameter D chosen to be very small, the terms on the rhs of (9a) are reduced to practically δ-functions and the double sum becomes $g(\mathbf{r})$ of the simulated macroscopic system.

However, by taking n to be large, we lose the advantage of an analytic representation of $g(\mathbf{r})$. Therefore one would desire to keep n small, say $n < 10$. On the other hand, the above model imposes an average density (3) fixed by L, and excludes the formation of random excess volumes per atom over that of the average atomic volume (v/n) within domains of a size of the order of a unit cell, or larger. To allow for the possibility of random excess volumes within such domains, more general spatial random processes must be considered. This is achieved here by including beside random displacements $\mathbf{s}$ also transitions between different types of local structure. Thus, assuming several possible local structures and associating again a lattice L_α with a local structure of type α, we can introduce an additional discrete, radially evolving, Markoffian process defined by a set $\mathbf{A} = \{\mathbf{A}_{\alpha\beta}\}$ of transition probabilities (per unit distance) between different local structures.

Formal complications in combining the continuous $\mathbf{s}$-process with the discrete $\mathbf{A}$-process are avoided by taking all L_αs to be commensurate, i.e. to have a common Bravais lattice, differing only by their sets of points $(\mathbf{a}_\sigma^{(\alpha)}, \sigma = 1, \ldots, n_\alpha)$ within the common unit cell. Thus $\mathbf{s}$ can specify a random relative displacement of any local structure irrespective of its type. A treatment of the case of incommensurate L_αs is given in the Appendix. Assuming the $\mathbf{s}$ and $\mathbf{A}$ processes to be mutually independent, we arrive at a combined structural diffusion–transition (SDT) equation

$$\frac{\partial \mathbf{P}}{\partial \mathbf{r}} = D\nabla_{\mathbf{s}}^2 \mathbf{P} + \mathbf{A}\mathbf{P}, \tag{12}$$

which is an extension of (4). Equation (12) has its analog in equations for temporal reaction–diffusion processes. Here $\mathbf{P}$, $\mathbf{A}$, and D are $l \times l$ matrices, with l the number of different local structures. The columns of $\mathbf{P} = \{\mathbf{P}_{\alpha\beta}(\mathbf{s}|r)\}$ are the conditional probabilities of finding at a distance r a local structure of type α, displaced by the amount $\mathbf{s}$ relative to a structure of type β at the origin. $\mathbf{A}$ is a matrix whose sum of terms of each column is zero:

$$\sum_\alpha \mathbf{A}_{\alpha\beta} = 0. \tag{13}$$

Putting $\mathbf{P} = e^{\mathbf{Ar}}\bar{\mathbf{P}}$, (12) is reduced to the diffusion equation

$$\frac{\partial \bar{\mathbf{P}}}{\partial r} = \bar{D}\nabla_{\mathbf{s}}^2 \bar{\mathbf{P}}, \qquad \bar{D} = e^{-\mathbf{Ar}} D e^{\mathbf{Ar}}. \tag{14}$$

which has the solution

$$\mathbf{P}(\mathbf{s}|r) = \frac{1}{v} e^{\mathbf{Ar}} \sum_{v} e^{-\bar{D}\mathbf{r}\mathbf{b}_v^2 e^{i\mathbf{b}_v \cdot s}}, \tag{15}$$

satisfying the boundary condition

$$\mathbf{P}(\mathbf{s}|r = 0) = \mathbf{I}\delta(\mathbf{s}),$$

where $\mathbf{I}$ is the $l \times l$ unit matrix. In the following we employ the simplification of assuming D to be a scalar, hence $\bar{D} = D$. By (13) $\mathbf{A}$ is a singular matrix whose eigenvalues are

$$\lambda_0 = 0 > \lambda_1 > \cdots > \lambda_{l-1}.$$

Consequently, we can write [31]

$$e^{\mathbf{Ar}} \equiv \mathbf{Q}(\mathbf{r}) = \mathbf{I} + \sum_{i=1}^{l-1} (e^{\lambda_i \mathbf{r}} - 1)\mathbf{Z}_i, \tag{16}$$

where $\mathbf{Z}_i$, $i = 1, \ldots, l-1$ are projection matrices (the "components" of $\mathbf{A}$), $\mathbf{Z}_i\,\mathbf{Z}_j = \delta_{ij}\,\mathbf{Z}_i$, with each $\mathbf{Z}_i$ satisfying also condition (13). The following calculations are restricted to $l = 2$, i.e. two different L_αs, $\alpha = 1, 2$ (two "states"). $\mathbf{A}$ has then the explicit form

$$\mathbf{A}_{11} + \mathbf{A}_{21} = 0, \quad -\mathbf{A}_{11} = \mathbf{A}_{21}$$
$$\mathbf{A}_{12} + \mathbf{A}_{22} = 0, \quad -\mathbf{A}_{22} = \mathbf{A}_{12}.$$

By detailed balance $\mathbf{A}_{12}p_2 = \mathbf{A}_{21}p_1$, hence

$$\frac{p_2}{p_1} = \frac{\mathbf{A}_{21}}{\mathbf{A}_{12}} \qquad \text{or} \quad -\mathbf{A} = \begin{pmatrix} a_2 & -a_1 \\ -a_2 & a_1 \end{pmatrix}; \quad (a_\alpha = \kappa_a p_\alpha) \tag{17}$$

where p_α is the probability of finding the local structure L_α at an arbitrary point $\mathbf{r}$. Thus, $\mathbf{A}$ has the eigenvalues $\lambda_0 = 0$, $\lambda_1 = -a_1 - a_2 = -\kappa_a$, and the component

$$\mathbf{Z}_1 = -\frac{1}{\kappa_a}\mathbf{A} = \begin{pmatrix} p_2 & -p_1 \\ -p_2 & p_1 \end{pmatrix}, \tag{18}$$

hence, by (16) and (18),

$$\mathbf{Q}(\mathbf{r}) = \mathbf{I} + (e^{-\kappa_a \mathbf{r}} - 1)\begin{pmatrix} p_2 & -p_1 \\ -p_2 & p_1 \end{pmatrix}. \tag{19}$$

The elements, $\mathbf{Q}_{\alpha\beta}(\mathbf{r})$, of this matrix are the conditional probabilities of finding a local structure α at $\mathbf{r}$, given a local structure β at the origin. Again, to allow for deviations at small $\mathbf{r}$ from a strictly Markoffian process, we make a generalization of $\mathbf{Q}(\mathbf{r})$, similar to the replacement of $D\mathbf{r}$ by the function $W(\mathbf{r})$ satisfying (5), to a matrix having the asymptotic form

$$\mathbf{Q}(\mathbf{r}) \sim e^{\mathbf{A}\mathbf{r}}, \quad r \to \infty; \qquad \mathbf{Q}'(\mathbf{r}) \to 0, \quad r \to 0.$$

In the particular case of two ''states,'' the exponent $\kappa_a r$ in (19) is replaced by a function $w(r)$ satisfying the asymptotic form

$$w \sim \kappa_a r, \quad r \to \infty; \qquad w'(r) \to 0, \quad r \to 0. \tag{5a}$$

Extending (2) to include several local structures L_α, the local density for a given local structure $(L_\alpha, \mathbf{s})$ is given now by

$$\rho(\mathbf{r}) = \rho(\mathbf{r}; \alpha, \mathbf{s}) = \sum_\mu \sum_{\sigma=1}^{n_\alpha} \delta(\mathbf{r} - \mathbf{a}_\mu - \mathbf{a}_\sigma^{(\alpha)} - \mathbf{s}), \tag{20}$$

and the average density is

$$\rho = \sum_\alpha p_\alpha \rho_\alpha, \quad \rho_\alpha = \frac{n_\alpha}{v} \tag{21}$$

where ρ_α is the average density of particles (points) in L_α.

Similarly, extending (8) and (9) to several Ls, we obtain for the pair distribution

$$\rho^2 g(\mathbf{r}) = \rho^2 g(\mathbf{r}; L, D, \mathbf{A}) = \sum_{\alpha\beta} \rho_\beta \mathbf{Q}_{\beta\alpha}(\mathbf{r}) p_\alpha \rho_\alpha \hat{g}_{\alpha\beta}(\mathbf{r}), \tag{22}$$

where

$$\hat{g}_{\alpha\beta}(\mathbf{r}) = \sum_\nu \Gamma_\alpha(\mathbf{b}_\nu)\Gamma_\beta^*(\mathbf{b}_\nu) e^{-W\mathbf{b}_\nu^2} \langle e^{i\mathbf{b}_\nu \cdot \mathbf{r}} \rangle_0, \tag{23}$$

with

$$\Gamma_\alpha(\mathbf{b}_\nu) = \frac{1}{n_\alpha} \sum_{\sigma=1}^{n_\alpha} e^{i\mathbf{b}_\nu \cdot \mathbf{a}_\sigma^{(\alpha)}}, \qquad |\Gamma_\alpha(\mathbf{b}_\nu)|^2 = C_\nu, \text{ etc.}$$

By the Poisson transformation, (23) has the alternative representation

$$\rho_\alpha \hat{g}_{\alpha\beta}(\mathbf{r}) = \frac{1}{n_\beta} \sum_{\sigma'=1}^{n_\beta} \sum_{\mu} \sum_{\sigma=1}^{n_\alpha} \frac{1}{(4\pi W)^{3/2}} \left\langle \exp\left[-\frac{(\mathbf{r} - \mathbf{a}_\mu - \mathbf{a}_\sigma^{(\alpha)} + \mathbf{a}_{\sigma'}^{(\beta)})^2}{4W} \right] \right\rangle_0 . \tag{23a}$$

$\rho_\beta \hat{g}_{\alpha\beta}$ can be interpreted as the particle density at $\mathbf{r}$, given the local structures L_α and L_β at the origin and at $\mathbf{r}$, respectively. As in the case of Eq. (9), Eqs. (22) and (23) apply only to $\mathbf{r} \neq 0$, since their rhs contains also contributions of self-correlations to the pair distribution.

The more general treatment (see Appendix) allowing for different L_αs to be incommensurate, leads to the same results (22) and (23) except that the cross terms vanish,

$$\hat{g}_{\alpha\beta} = 0, \quad L_\alpha, L_\beta \text{ incommensurate.} \tag{23i}$$

4. RANDOM LOCAL VOIDS AND PAIR CORRELATIONS

The foregoing model enables us to define voids as a random excess volume, as follows: Let $L = (L_1, L_0)$ be a set of two local structures – a lattice L_1 and the empty lattice L_0 (where $n_0 = 0$, i.e. $\rho_0 = 0$), with the respective frequencies p_1, p_0. We have then $\rho = p_1 \rho_1$, with ρ the average density and ρ_1 the density of structure L_1. Writing

$$\rho_1 \hat{g}_{11} = G_1(\mathbf{r}) = \rho_1 \sum_\nu C_\nu e^{-W\mathbf{b}_\nu^2} \langle e^{-i\mathbf{b}_\nu \cdot \mathbf{r}} \rangle_0, \tag{24}$$

we have

$$G(\mathbf{r}) = \mathbf{Q}_{11}(\mathbf{r}) G_1(\mathbf{r}), \quad \mathbf{Q}_{11}(\mathbf{r}) = p_1 + e^{-w} p_0; \qquad g(\mathbf{r}) = \frac{1}{\rho} G(\mathbf{r}), \quad \mathbf{r} \neq 0. \tag{25}$$

Hence, with $p_1 = \rho/\rho_1$, $p_0 = 1 - p_1$,

$$\rho g(\mathbf{r}) = [\rho + e^{-w} \Delta\rho] g_1(\mathbf{r}), \quad g_1(\mathbf{r}) = G_1(\mathbf{r})/\rho_1, \quad \mathbf{r} \neq 0. \tag{26}$$

where $\Delta\rho = \rho_1 - \rho$. With $v = \rho^{-1}$ and $v_1 = \rho_1^{-1}$ the volume per particle in the given system and in L_1, respectively, $\Delta v = v - v_1$ is an average random excess volume of voids defined with respect to the volume occupied by a globally ordered structure (L_1). Clearly, this definition of voids depends on the choice of L_1, which reflects our limited ability to infer a unique global pattern from local atomic configurations. The ordered structure has no random excess volume, irrespective of the notions of excluded volume of a particle or empty space between particles.

By (25), $\mathbf{Q}_{11}(\mathbf{r})$ has the asymptotic forms

$$\mathbf{Q}_{11}(\mathbf{r}) = \begin{cases} p_1, & r \to \infty \\ 1, & r \to 0 \end{cases},$$

and correspondingly, by (24) and (25),

$$\begin{aligned} &G_1(\mathbf{r}) = \rho_1, \quad G(\mathbf{r}) = \rho, \quad r \to \infty; \\ &G_1(\mathbf{r}) \sim G(\mathbf{r}) = \delta(\mathbf{r}), \quad r \to 0; \end{aligned} \tag{27}$$

with the correct asymptotic behavior. Note that since $\Delta v > 0$, $G < G_1$ for all $\mathbf{r}$ (where $g > g_1$), which means that in a system free of random voids (L_1, D), the neighborhood shell density $G_1(\mathbf{r})$ is larger than the density $G(\mathbf{r})$ in a system with random voids (L_1, L_0, D). Rewriting (26) in the form

$$G - \rho = (\rho + \Delta\rho e^{-w})(G_1 - \rho_1)/\rho_1 + \Delta\rho e^{-w}, \tag{26a}$$

using the series representation

$$(G_1 - \rho_1)/\rho_1 = \sum_{\nu}{}' C_\nu e^{-W\mathbf{b}_\nu^2} \langle e^{i\mathbf{b}_\nu \cdot \mathbf{r}} \rangle_0, \tag{9a}$$

with the primed summation sign denoting omission of the $\nu = 0$ term, we note that the radial density distribution includes a continuous contribution $\Delta\rho e^{-w}$ of void density deficiency, beside the contributions of individual neighborhood shells.

In the following applications we assign to the **A**-process the same functional form (10) of spatial decay as in the D-process, by putting

$$w = \kappa_a r_a \omega\left(\frac{r}{r_a}\right). \tag{28}$$

The constant r_a is a measure of an average size of domains with dominant L_1 structure, free of random voids. As seen from (26), since for $r < r_a$ $\mathbf{w}$ is small, approaching zero when $r \to 0$, the neighborhood shell density approaches $\rho_1 g_1$, whereas for large $r \geq r_a$, when $w \to \infty$, this density approaches ρ.

Fitting (24) (via (26)) to experimental $g(\mathbf{r})$ data requires now adjustment of the parameters defining the lattice L_1, and of four additional parameters, D, r_0, κ_a, and r_a, keeping fixed $W_0 = 10^{-4}$. Resulting representations of $g(\mathbf{r})$ for liquid Argon and liquid Aluminum, obtained previously using (11.2) and a simple estimate of random excess volume, consistent with limit values of the radial distribution, are given in the respective Figs. 1 and 2 of ref. [8]. The corresponding relative excess volume (density deficiencies), $\Delta v/v_1$, was, respectively, 12% (Ar) and 9% (Al) of the total volume, where L was a lattice with $n = 4$ (the number of points per unit cell).

5. THE SCATTERING FUNCTION

Given G(r) via the analytic expressions (23) and (23a), the scattering function can be evaluated numerically from

$$S(\mathbf{k}) = \int (G(\mathbf{r}) - \rho) e^{i\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{r} \tag{29}$$

by fast Fourier transform (FFT). Note that for small **r** we have to use the representation (23a), and can replace the $\mu = 0$, $\sigma = \sigma'$, term by the correct $\delta(\mathbf{r})$ function term of self-correlations. It is represented to a good approximation by the former term [10], which contributes practically the correct value unity to (29), with an error of order 1%.

Substituting (26a) into (29) and performing integration term by term, we obtain $S(\mathbf{k})$ as a series

$$S(\mathbf{k}) = \sum_{\nu} S_\nu(\mathbf{k}), \tag{30}$$

where the terms

$$S_\nu(\mathbf{k}) = \int (\rho + \Delta\rho e^{-w}) e^{-W\mathbf{b}_\nu^2} \langle e^{i\mathbf{b}_\nu \mathbf{r}} \rangle_0 e^{i\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{r}, \quad \nu \neq 0, \tag{30n}$$

represent contributions of the respective shells of the reciprocal lattice L^* to the scattering, and

$$S_0(\mathbf{k}) = \int \Delta\rho e^{-w} e^{i\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{r}, \tag{30.0}$$

forming a background contribution to the scattering, is due to the random voids and is proportional to their density deficiency $\Delta\rho$.

By definition $S(\mathbf{k})$ is a positive function of **k**. By construction (due to our choice of functional form) this holds also for each term $S_\nu(\mathbf{k})$ in (30) (see [27,28]). Hence each $S_\nu(\mathbf{k})$ can be viewed as an (unnormalized) distribution of **k**. Defining a composite width function

$$\Omega(r; \kappa_\nu, \kappa_\alpha) = \sum_i \kappa_{\nu i} r_i \omega(r/r_i) + \kappa_a r_a \omega(r/r_a), \quad \kappa_{\nu i} = D_i \mathbf{b}_\nu^2, \tag{31}$$

with $\omega(x)$ given by (11), the integral

$$I(k; \kappa_\nu, \kappa_a) \equiv \int_0^\infty e^{-\Omega(\mathbf{r}; \kappa_\nu, \kappa_a)} \cos kr \, dr, \quad \kappa_\nu \equiv \{\kappa_{\nu 1}, \kappa_{\nu 2}, \ldots\} \tag{32}$$

is symmetric in k, peaked around $k = 0$ with a maximum $\mathbf{I}(0; \kappa_\nu, \kappa_a)$ and is integrable over the entire range $-\infty < k < \infty$. When Ω consists of a single ω term, the integral in (32) can be evaluated analytically [10]. From the inversion formula for (32),

$$e^{-\Omega(\mathbf{r}; \kappa_\nu, \kappa_a)} = \frac{1}{2\pi} \int_0^\infty I(k; \kappa_\nu, \kappa_a) \cos kr \, dk, \tag{33}$$

one can obtain the dispersion of k,

$$\langle k^2 \rangle = \int_0^\infty I(k; \kappa_\nu, \kappa_a) k^2 dk \Big/ \int_0^\infty I(k; \kappa_\nu, \kappa_a) \, dk, \tag{34}$$

using the relation

$$\langle k^2 \rangle = -\left[\frac{\partial^2}{\partial r^2} e^{-\Omega(\mathbf{r};\kappa_\nu,\kappa_a)} \Big/ e^{-\Omega(\mathbf{r};\kappa_\nu,\kappa_a)} \right]_{\mathbf{r}=0}. \tag{35}$$

In particular, substituting for $\omega(x)$ in (31) either (11.1) or (11.2), we obtain

$$\langle k^2 \rangle = \sum_i \frac{\kappa_{\nu i}}{r_i} + \frac{\kappa_a}{r_a}. \tag{36}$$

It follows now from (30n) and (30.0) that the $S_\nu(\mathbf{k})$ can be expressed in terms of the $I(k;\,\kappa_\nu,\,\kappa_a)$. Writing

$$K_\nu(k;\kappa_\nu,\kappa_a) = 4\pi \frac{I(k-b_\nu;\kappa_\nu,\kappa_a) - I(k+b_\nu;\kappa_\nu,\kappa_a)}{2kb_\nu}, \tag{37}$$

we obtain

$$S(\mathbf{k}) = \sum_\nu{}' C_\nu e^{-W_0\mathbf{b}_\nu^2}[\rho K_\nu(k;\kappa_\nu,0) + \Delta\rho K_\nu(k;\kappa_\nu,\kappa_a)] + \Delta\rho K_0(k;0,\kappa_a), \tag{38}$$

where

$$K_0(k;0,\kappa_a) = \lim_{\mathbf{b}_\nu \to 0} K_\nu(k;\kappa_\nu,\kappa_a) = \frac{4\pi}{k}\frac{\partial I(k;0,\kappa_a)}{\partial k}. \tag{39}$$

By the foregoing considerations we see from (37) that the K_ν terms in (38) contribute to $S(\mathbf{k})$ peaks around $k \approx b_\nu$ – the L* shell positions, with progressively increasing widths (36) and decreasing heights, and the K_0 term contributes an additional background distribution proportional to the density deficiency $\Delta\rho$ due to random voids.

Fitting $S(\mathbf{k})$ data [32] for liquid Aluminum to the SDT model are shown in Fig. 2, with the corresponding g(r), calculated directly from the analytic expressions (26), given in Fig. 3. We have chosen a width function W with two terms in the (10′) representation, using the form (11.1) for $\omega(x)$. Thus, the total set of adjusted parameters is (D_1, r_1, D_2, r_2, κ_a, $\{L\}$) where $\{L\}$ is a set defining the unit cell of L, amounting to $3(n+1)$ parameters, where n is the number of points in a unit cell. (We have put $\mathbf{r}_a = \mathbf{r}_2$ in order to introduce correlations between the **A**- and **D**-process). Several fitting curves by simulated annealing, starting from an fcc L with $n = 1, 2, 8$, are shown in the two figures. When $n > 1$ there appear spikes in curves for $S(\mathbf{k})$ in the small k range $k < k_{\max}$ – position of the maximum of $S(\mathbf{k})$, barely apparent in the data. These spikes are an artifact of the model lattice sum representation of $g(\mathbf{r})$, appearing when the unit cell of L contains more than one point, which entails a unit cell of smaller size than $k_{\max}$ for the reciprocal lattice L*. Negative values for the $S(\mathbf{k})$ curves in this range, where $S(\mathbf{k})$ becomes very small, of the order of 10^{-2}, are due to limitations of the FFT procedure and should be absent from a more accurate numerical evaluation of (29). The slight rise of $S(\mathbf{k})$ towards $k \to 0$ might have physical significance, as found from careful analysis of scattering data in this region [33].

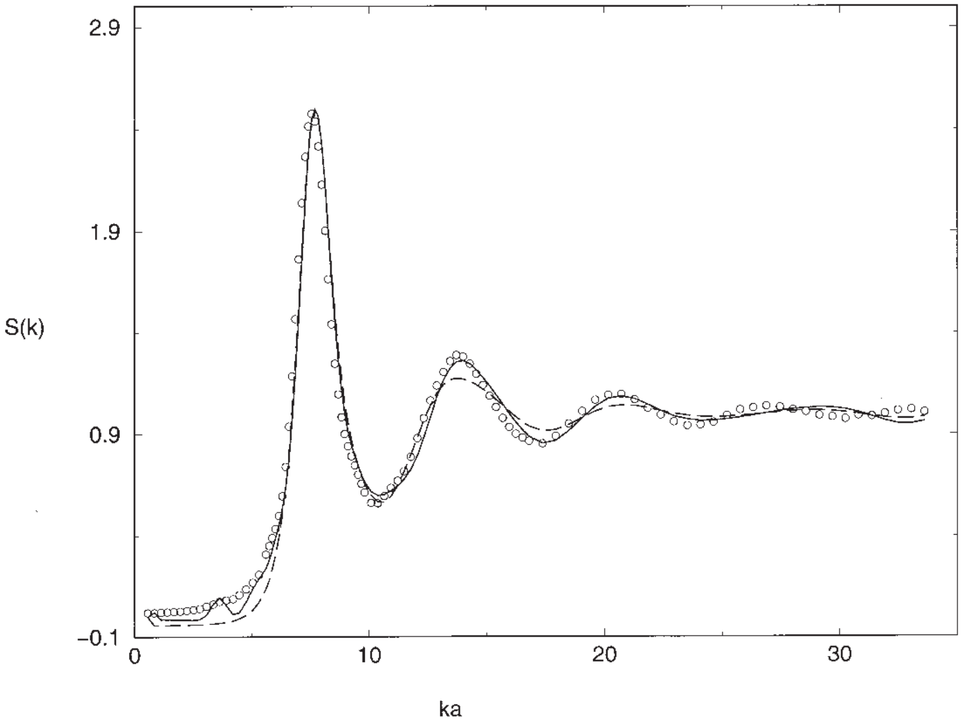

FIGURE 2 $S(\mathbf{k})$ of liquid aluminum. Circles: experimental points; solid line: L ($n=8$); dashed line: L ($n=1$) (see text).

Another discrepancy is an increasing mismatch and phase shift of the oscillations in the high k range. It seems that the oscillations beyond the first peak of $S(\mathbf{k})$ are mainly a consequence of the steep drop of $g(\mathbf{r})$ to zero at small $\mathbf{r}$, due to the strong short range repulsive forces, and that both the shift and damping of the oscillations in the model $S(\mathbf{k})$ reflect a failure to reproduce a sufficiently sharp drop in $g(\mathbf{r})$.

The resulting fractional excess volumes, $\Delta v/v_1 = \Delta\rho/\rho$, for 3 Ls are as follows: 20% ($n=1$), 12% ($n=2$), 9.4% ($n=8$), showing approach toward a more ordered structure with increasing n, illustrating the dependence of our definition of random voids on the choice of the ordered reference structure, with a more complex L approaching more closely that of the modeled disordered system (the liquid). An extreme example is a lattice with a huge unit cell ($N \sim 10^3 - 10^4$) produced by the reverse Monte Carlo method. Note that compared to the solid Al crystal, the liquid volume is larger by 14.3% [32], implying that the liquid model lattice L ($n=8$) is expanded compared to L_{cr} – the crystal lattice.

6. LIMIT POINTS IN STRUCTURE SPACE

Consider now the limit $D \to 0$, when the D-process has only a small effect, while keeping the **A**-process, i.e. $\kappa_a \neq 0$. As seen from (23a), $g(\mathrm{r})$ becomes a sum of sharp peaks with equal dispersion W_0, situated at the neighborhood shell positions of L_1.

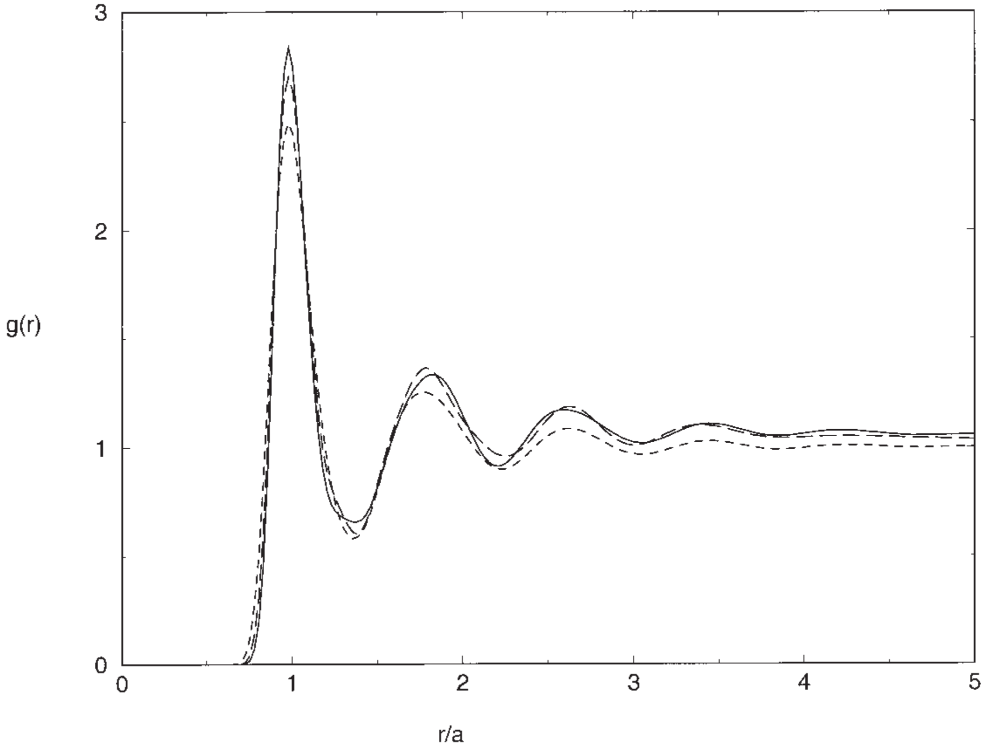

FIGURE 3 $g(r)$ of liquid aluminum from fitting to $S(\mathbf{k})$ data. Solid line: L ($n=8$); long dashed line: L ($n=2$); dashed line: L ($n=1$) (see text).

This corresponds to long range order in a crystalline powder. However, because of the **A**-process the average shell density decreases from ρ_1 to ρ with increasing r, at a radial rate κ_a, as can be seen from (26a). In contrast, the peaks in $S(\mathbf{k})$ have a nonzero dispersion κ_a/r_a as long as $r_a<\infty$, i.e. as long as the size of the coherently diffracting domains is finite.

Writing (26a) as

$$G-\rho=(\rho/\rho_1)(G_1-\rho_1)+\Delta G, \qquad \Delta G=(\Delta\rho/\rho_1)e^{-w}G_1,$$

we see that the incremental contribution ΔG to $G(\mathrm{r})$ leads to a corresponding contribution to $S(\mathbf{k})$. Putting $\omega(x)\sim x$, we obtain for small k

$$\Delta S(\mathbf{k})=4\pi\Delta\rho\kappa_a\left[\sum_{\nu}{}' e^{-W_0\mathbf{b}_\nu^2}\frac{C_\nu}{[\kappa_a^2+(b_\nu-k)^2][\kappa_a^2+(b_\nu+k)^2]}+\frac{1}{(\kappa_a^2+k^2)^2}\right]. \tag{40}$$

It consists of broadened peaks of effective width κ_a at the neighborhood shells of the reciprocal lattice L_1^*, and an additional background distribution around the origin. All are proportional to $\Delta\rho$, thus due to the random voids trapped in an otherwise crystalline structure. The effect of void distribution can be compared to a background contribution due to a finite size κ_a^{-1} of the crystals to the scattering [34].

One could associate the $D \to 0$ limit with an "ideal glass" state [35], which is a state implied by extrapolation from a sequence of glass samples formed by increasingly slow cooling rates of a supercooled liquid. Such a state might correspond to a distribution of crystallites whose average linear size is of the order of κ_a^{-1}, while the space between the crystallites makes the excess volume, given by the relative density deficiency $\Delta\rho/\rho$.

In the liquid state, where $\mathbf{r}_a\kappa_a > 1$, the concept of micro-crystallites (or para-crystals [9]) looses its meaning as extended ordered sets of atoms and should be understood only as reference structures for the relative positions (distances, bond and plane angles, etc.) of neighboring atoms. Accordingly, D and κ_a refer to suitably averaged local atomic configurations. As mentioned above, the relative density deficiency $\Delta\rho/\rho$ can still serve as a measure of the fraction of random voids in the liquid, but depends on the choice of the reference structures.

7. CONCLUDING REMARKS

Parametrized analytic representations of molecular correlations serve as models enabling analysis of relationships between structure and macrostates of the system. The models developed in the foregoing have two essential ingredients: a small number of local structure elements, and spatial random processes specified by a small set of parameters defining the correlations between these elements. The two parts are intimately connected: The definition of the correlations between structure elements at different localities implies that full correlations correspond to global (macroscopic) order. This is indeed obeyed in the foregoing examples. For local lattices L related by a relative displacement $\mathbf{s}$, the formation of global order (i.e. crystallization) results from full coherence throughout space between local structures, corresponding to $D = 0$. For several different types of local lattices related by transition probabilities, full correlation corresponds to $\kappa_a = 0$ in (17), i.e. zero transition probabilities, which implies that the system contains macroscopic regions, each consisting of a single lattice structure. Any other conceived local elements not related to lattice structures, such as, say, icosahedra, would require defining corresponding random processes conforming to the above conditions. In the case of local icosahedral structures this turns out to be possible by considering random displacements of a lattice in six-dimensional space [36].

The analysis of the relation between structure and disorder in condensed systems, presented by the foregoing models, is incomplete, as follows from consideration of entropy in terms of ensembles of energy states [12], requiring also knowledge of molecular interactions potentials in addition to pair distribution data.

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APPENDIX

Incommensurate Local Lattices

When several incommensurate local lattices L_α are assumed, this requires redefining a relative displacement $\mathbf{s}^\alpha$ for each L_α with respect to a common reference lattice $\bar{L}$, which we choose to be a simple cubic lattice with unit length cell edges, as follows: Writing $\mathbf{s}^\alpha$ in terms of the vectors defining the unit cell of L_α, $\mathbf{s}^\alpha = \sum_{\mathbf{k}=1}^{3} s_{\mathbf{k}}^\alpha \mathbf{a}_{\mathbf{k}}^\alpha, 0 \le s_{\mathbf{k}}^\alpha < 1,$ we define the set $\bar{\mathbf{s}} \equiv (s_1^\alpha, s_2^\alpha, s_3^\alpha)$ as the Cartesian coordinates of the displacement inside the unit cubic cell of $\bar{L}$. Thus, the transformation formula from volume elements in $\mathbf{s}^\alpha$ to $\bar{\mathbf{s}}^\alpha$ is

$$d^3\mathbf{s}^\alpha = \frac{\partial(\mathbf{s}^\alpha)}{\partial(\bar{\mathbf{s}}^\alpha)} d^3\bar{\mathbf{s}}^\alpha = \det|\mathbf{a}_{\mathbf{k}i}^\alpha| d^3\bar{\mathbf{s}}^\alpha = v_\alpha d^3\bar{\mathbf{s}}^\alpha, \tag{A1}$$

where $\mathbf{a}_{\mathbf{k}i}^\alpha$, $i = 1, 2, 3$ are the Cartesian coordinates of $\mathbf{a}_{\mathbf{k}}^\alpha$.

We now rewrite (20), the local density for a given local structure $(L_\alpha, \bar{\mathbf{s}})$, by

$$\rho(\mathbf{r}; \alpha, \mathbf{s}) = \sum_{\sigma,\,\mu} \delta(\mathbf{r} - \mathbf{r}^{\alpha}_{\sigma,\,\mu}(\bar{\mathbf{s}})), \tag{A2}$$

where μ runs over all cells and σ runs over all atoms of type α in the unit cell of $\bar{L}$, and

$$\mathbf{r}^{\alpha}_{\sigma,\,\mu}(\mathbf{s}) = \mathbf{a}^{\alpha}_{\sigma+\mu} + \mathbf{s}^{\alpha}. \tag{A3}$$

For the pair distribution

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \langle \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \rangle$$

the average is now over all local states, $(\alpha, \bar{\mathbf{s}}_1)$ at r_1 and $(\beta, \bar{\mathbf{s}}_2)$ at r_2. The local states are correlated by the transition probability $\mathbf{P}_{\beta\alpha}(\bar{\mathbf{s}}|\mathbf{r})$, $\bar{\mathbf{s}} = \bar{\mathbf{s}}_2 - \bar{\mathbf{s}}_1$, which is the conditional probability of finding at a distance r a local structure of type β, displaced by the amount $\bar{\mathbf{s}}$ relative to a structure of type α at the origin. Hence

$$\begin{aligned} n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{\beta,\,\alpha} p_\alpha \iint d^3\mathbf{s}_1\, d^3\mathbf{s}_2\, \rho(\mathbf{r}_1; \alpha, \bar{\mathbf{s}}_1)\rho(\mathbf{r}_2; \beta, \bar{\mathbf{s}}_2)\mathbf{P}_{\beta\alpha}(\bar{\mathbf{s}}_2 - \bar{\mathbf{s}}_1) \\ &= \sum_{\beta,\,\alpha} p_\alpha \frac{1}{v_\alpha v_\beta} \iint d^3\mathbf{s}^\alpha d^3\mathbf{s}^\beta \sum_{\sigma\alpha,\,\mu\alpha}\ \sum_{\sigma\beta,\,\mu\beta} \delta(\mathbf{r}_1 - \mathbf{a}_{\sigma\alpha+\mu\alpha} - \mathbf{s}^\alpha)\delta(\mathbf{r}_2 - \mathbf{a}_{\sigma\beta+\mu\beta} - \mathbf{s}^\beta) \\ &\quad \times \mathrm{P}_{\beta\alpha}(\bar{\mathbf{s}}_2 - \bar{\mathbf{s}}_1|\mathbf{r}) \end{aligned} \tag{A4}$$

where

$$\mathbf{P}_{\beta\alpha}(\bar{\mathbf{s}}_2 - \bar{\mathbf{s}}_1|\mathbf{r}) = \mathbf{Q}_{\beta\alpha}(\mathbf{r}) \sum_{\nu} e^{-W(\mathbf{b}^\beta_\nu)^2} e^{i(\mathbf{b}^\beta_\nu\cdot\mathbf{s}^\beta_2 - \mathbf{b}^\alpha_\nu\cdot\mathbf{s}^\alpha_1)}. \tag{A5}$$

We have assumed here, as before in Section 4, that the $\bar{\mathbf{s}}$ process is independent of the type of local structure. Performing integration and further averaging over all orientations of $\mathrm{r} = \mathrm{r}_2 - \mathrm{r}_1$ and all positions in space of r_1 (averaging symbolized by $\langle\rangle_{0,\,V}$), we obtain

$$n^{(2)}(\mathbf{r}) = \sum_{\alpha\beta} \mathbf{P}_\alpha \mathbf{Q}_{\beta\alpha}(\mathbf{r}) \frac{1}{v_\alpha v_\beta} \sum_{\nu} e^{-W(\mathbf{b}^\beta_\nu)^2} \sum_{\sigma\alpha} \sum_{\sigma\beta} e^{i(\mathbf{b}^\beta_\nu\cdot\mathbf{a}^\beta_\sigma - \mathbf{b}^\alpha_\nu\cdot\mathbf{a}^\alpha_\sigma)} \langle e^{i(\mathbf{b}^\beta_\nu\cdot\mathbf{r}_2 - \mathbf{b}^\alpha_\nu\cdot\mathbf{r}_1)} \rangle_{o,\,V} \tag{A6}$$

Note that from each sum $\sum_\mu$ over cells, only the term for the one cell with the point r inside it remains after integration. Here

$$\langle e^{i(\mathbf{b}^\beta_\nu\cdot\mathbf{r}_2 - \mathbf{b}^\alpha_\nu\cdot\mathbf{r}_1)} \rangle_{o,\,V} = \langle e^{i\mathbf{b}^\beta_\nu\cdot\mathbf{r}} \rangle_o \frac{1}{V} \int e^{i(\mathbf{b}^\beta_\nu - \mathbf{b}^\alpha_\nu)\cdot\mathbf{r}_1} d^3\mathbf{r}_1 = \frac{\sin b^\beta_\nu r}{b^\beta_\nu r} \delta(\mathbf{b}^\beta_\nu - \mathbf{b}^\alpha_\nu), \tag{A7}$$

where

$$\delta_{\mathbf{b}} = \begin{cases} 0, & \mathbf{b} \neq 0 \\ 1, & \mathbf{b} = 0 \end{cases}.$$

Hence, if the two lattices $L_\alpha \neq L_\beta$ are mutually incommensurate, all cross terms drop except for the $\nu = 0$ term. Hence

$$n^{(2)}(\mathbf{r}) = \sum_{\alpha\beta} \rho_\alpha \rho_\beta \mathbf{Q}_{\beta\alpha}(\mathbf{r}) \sum_{\nu} \Gamma^{\beta}(\nu) \Gamma^{\alpha}(\nu)^* e^{-W(\mathbf{b}_\nu^\beta)^2} \frac{\sin b_\nu^\beta r}{b_\nu^\beta r} \delta(\mathbf{b}_\nu^\beta - \mathbf{b}_\nu^\alpha) \tag{A8}$$

where

$$\Gamma^{(\alpha)}(\nu) = \frac{1}{n_\alpha} \sum_{\sigma\alpha} e^{i\mathbf{b}_\nu^\alpha \cdot \mathbf{a}_\sigma^\alpha}, \quad \Gamma^{\alpha}(0) = 1;\ \text{etc.}$$

Thus, for mutually incommensurate lattices cross terms $\alpha \neq \beta$ drop out from (A8).