Multi-theta distributions of local structures in condensed matter: a new route to triplet and

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Abstract. Triplet and higher-order molecular distributions in condensed media are obtained from pair distributions by extension of a method based on the notion of spatial Markoffian-like processes for local ordered structures. The extension is achieved by defining the spatial process in terms of multivariate theta distributions, in full analogy with multivariate distributions of a temporal Gaussian process. This result enables one to obtain effective pair potentials from empirical radial distributions by solving the BKY integral equation relating the pair potential to pair and triplet distributions. The relative merits of a microscopic description of the condensed system in terms of effective pair potentials or in terms of local structures are discussed.

1. Introduction and summary

The radial distribution function $g(r)$ provides the most direct experimental information, available mainly through scattering data, about the spatial arrangement of the atoms in condensed non-crystalline systems. However, by itself $g(r)$ constitutes only very partial information on the atomic configurations in such phases. In contrast, a computer simulation gives us the fullest possible information on the atomic configurations, but it has to rely on assumed intermolecular potentials in order to determine the trajectories in molecular dynamics or the energy distribution in Monte Carlo calculations.

In principle, when the molecules interact only via pair potentials, complete information on the atomic configurations can be extracted from $g(r)$ alone, since by classical statistical mechanics all higher-order molecular distributions $g^{(n)}$, $n > 2$, are uniquely determined by $g \equiv g^{(2)}$ (Abe 1959, Stell 1964). However, in practice we can know $g^{(n)} = g^{(n)}[g]$ only approximately, and even that, at present, reasonably well only for $n = 3$.

Nevertheless, a knowledge of $g^{(3)}$ seems to provide much additional information necessary for more refined calculations of structural properties. In recent years several approximations have been devised, which are more accurate than the superpositon approximation (and the more recent convolution approximation, Jackson and Feenberg 1962, Ichimaru 1970) and have proved useful in several respects: Haymet *et al* (1981a, b) have used a truncated diagrammatic expansion of $g^{(3)}$ in terms of g and thus could find the pair potential $u(r)$ from $g(r)$ of simple fluids by solving the BKY integral equation involving g, $g^{(3)}$ and u. Higher-order $g^{(n)}$ can be expressed also in terms of direct

correlation functions $c^{(n)}$ (see e.g. Stell 1964, Baxter 1971) which play a key role in density functional theories of inhomogeneous fluids, in relation to derivation of improved integral equations for g and in theories of freezing. Rosenfeld (1989) has obtained $c^{(n)}$, $n \geq 3$, for hard-sphere systems from consideration of general constraints imposed by the exclusion volume on the spatial configuration of the spheres. His results for $c^{(3)}$ have been recently supported by extensive Monte Carlo simulations of hard-sphere systems near freezing (Rosenfeld et al 1990). The function $c^{(3)}$ determines third-order corrections to the free energy of crystal phases (see e.g. Barrat et al 1987), and hence is crucial in determining the freezing transition.

In this article we will present a new method for obtaining all higher $g^{(n)}$, and in particular $g^{(3)}$, from $g(r)$ data. The method is an extension of a certain modelling of $g(r)$ that is derived from the notion of a diffusion-like spatial random process for local structures in a non-crystalline phase (Baer 1977, 1979, 1987). This 'structural diffusion' process is defined in terms of the pair distribution of local ordered structures (the 'structural' pair distribution), from which $g(r)$ is uniquely determined.

The form of the structural pair distribution (a trivariate theta function, see below) suggests generalization to a random process defined by an hierarchy of multiplet distributions uniquely related to the pair distribution. Correspondingly we obtain an explicit expression for all higher-order molecular distributions $g^{(n)}$, whose numerical values are uniquely determined from those of the radial distribution $g(r)$. In particular we give an expression for $g^{(3)}$ in terms of the parameters characterizing $g(r)$. As mentioned above, $g^{(3)}$ can be utilized in a BKY integral equation to obtain an effective pair potential. We will consider the question of uniqueness and characteristics of such a potential in relation to the assumed local structures of the structural diffusion model. Work on numerical solution of the integral equation for $u(r)$ from typical $g(r)$ functions for simple monoatomic liquids will be published elsewhere.

2. Molecular and structural pair distributions

The modelling of radial distribution functions of liquids and amorphous solids in terms of local ordered structures related by a spatial Markoffian-type process (Baer 1977, 1979) provides a parametrized analytic expression for $g(r)$ that is both formally concise and suggestive of the local spatial arrangement of the atoms. The expression for $g(r)$, given as a sum over the points of the reciprocal of a given lattice L characteristic of the local structure, is

$$g(r) = \sum_{\nu} C_{\nu} \, e^{-Wb_{\nu}^2} \, \frac{\sin b_{\nu} r}{b_{\nu} r}. \tag{1}$$

This is based on the assumption that two local lattice structures L at different points in space can differ by a certain relative displacement s in 'structure' space and that this displacement obeys a certain spatial Markoffian-type process in s space. In the following we consider only the simplest case of L periodic in 3D space and s a simple translation of L.

The probability density $P(s|r)$ for such a process at a separation r between two localities is obtained in the form

$$P(s|r) = \frac{1}{v} \sum_{\nu} \exp(-Wb_{\nu}^2 + i\boldsymbol{b}_{\nu} \cdot \boldsymbol{s}) \tag{2}$$

where

$$\boldsymbol{b}_\nu = \sum_{i=1}^{3} \nu_i \boldsymbol{b}_i \qquad \nu_i = 0, \pm 1, \pm 2, \ldots \tag{3}$$

are the position vectors of the reciprocal lattice points, v is the volume of the unit cell of L and $W = W(r)$ is a monotonic, asymptotically linear, function of r,

$$W(r) \sim Dr \qquad r \to \infty. \tag{4}$$

The constant D, termed the 'structural diffusion coefficient', serves as a measure of the radial rate of decay of coherence between local structures. The RHS of (2) is the periodic solution of a diffusion-type equation for P in s space. It is the well known Fourier series representation of a theta function (see e.g. Bellman 1961) and is fully analogous to the Fourier integral representation of the Gaussian distribution function

$$(4\pi w)^{-1/2} \exp\left(-\frac{x^2}{4w}\right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-wy^2 + ixy} \, dy. \tag{5}$$

An alternative representation of the theta function as a sum of Gaussians corresponding to the LHS of (5) has the form

$$P(s|r) = (4\pi W)^{-3/2} \sum_\mu \exp\left(-\frac{|a_\mu - s|^2}{4W}\right) \tag{2'}$$

where the sum in (2') now extends over the lattice points, a_μ, of the primitive lattice of L. Equation (2') is obtained by a transformation of (2) via the Poisson sum formula.

It is clear that a representation of $g(r)$ by (1) can be made increasingly accurate by choosing L to be a sufficiently complex lattice or by extending structure space to higher dimensions (Baer 1987). Nevertheless in recent calculations, using a simple local lattice L in (1), it was possible to reproduce with good accuracy $g(r)$ data available from simulation and scattering experiments for several amorphous solid and liquid metal systems (Canessa *et al* 1988, Baer *et al* 1988, Lopez and Silbert 1989, Baer *et al* 1990). The success of the representation of $g(r)$, based on such a seemingly restricted view of the structure of liquid and amorphous systems, is supported by certain general considerations (Baer and Silbert 1986, Baer 1988) entirely independently of an assumed local lattice and leading to a general representation of $g(r)$ of the form (1). Thus (1) can be considered as a basis for theoretical studies while also being practically useful.

3. Higher-order distributions

An extension of the foregoing methods of modelling $g(r)$ to higher $g^{(n)}$ requires first an expression for the multiplet distribution of the 'local structures' $s_1, s_2, \ldots, s_n$ at n localities $r_1, r_2, \ldots, r_n$. However, we note that any attempt to extend the method of spatial Markoffian processes to distributions at more than two localities encounters the difficulty of a restriction to sequential ordering of the points in space. Such an ordering is natural in temporal processes but useless for spatial processes that are not evolving radially. Nevertheless, there exist generalizations of certain temporal Markoffian processes where the ordering becomes inessential. An example of such a process is the stationary Gaussian process (see e.g. Van Kampen 1981) which can be readily transcribed into the spatial case. By analogy with the generalization of (5) to a multivariate Gaussian distribution, we can generalize (2) to an nth-order distribution of local structures at n different points in space:

$$P^{(n)}\begin{pmatrix} s_1, s_2, \ldots, s_n \\ r_1, r_2, \ldots, r_n \end{pmatrix} = \frac{1}{v^n} \sum_{\nu_1 + \nu_2 + \ldots + \nu_n = 0} \exp\left(\sum_{i<j} W(r_{ij}) \boldsymbol{b}_{\nu_i} \cdot \boldsymbol{b}_{\nu_j} + i \sum_k \boldsymbol{b}_{\nu_k} \cdot s_k\right). \tag{6}$$

The multiple sum in (6) extends over the points of the reciprocal lattice L, with the restriction on the sums implying an independent summation over the position vectors of $n - 1$ points with respect to an nth point. The RHS of (6) is the Fourier series representation of a multi-$(3(n - 1)$ dimensional-) theta function (see Krazer 1903), which has also an alternative representation as a multiple sum of multi-Gaussian functions summed over lattice points. Such a multiple sum is a straightforward generalization of (2′) (see section 4).

It is now possible to obtain all $g^{(n)}$ directly from $P^{(n)}$ given by (6). We will illustrate this in explicit form for $n = 3$. Writing $P^{(3)}$ specifically as $P^{(3)}(s_1, s_2, s_3 | r_{12}, r_{13}, r_{23})$, we obtain for the molecular triplet distribution

$$n^{(3)}(r_1, r_2, r_3) = \int \int \int d^3s_1 \, d^3s_2 \, d^3s_3 \, P^{(3)}(s_1, s_2, s_3 | r_{12}, r_{13}, r_{23})$$
$$\times \rho(r_1, s_1)\rho(r_2, s_2)\rho(r_3, s_3) \tag{7}$$

where $\rho(r, s)$ are local singlet molecular densities given by

$$\rho(r, s) = \sum_\tau \delta(r - a_\tau - s) \qquad a_\tau = a_\mu + a_\sigma. \tag{8}$$

We use here the index set $\tau = (\mu, \sigma)$ to count all lattice points, were μ counts the unit cells and σ counts the points within a single cell. Thus the τ-summation is understood as a double summation, over both μ- and σ-sets. Substituting (8) and (7), we obtain

$$n^{(3)}(r_1, r_2, r_3) = \sum_{\sigma_1, \sigma_2, \sigma_3} P^{(3)}(r_1 - a_{\sigma_1}, r_2 - a_{\sigma_2}, r_3 - a_{\sigma_3} | r_{12}, r_{13}, r_{23}). \tag{9}$$

We have utilized here the fact that since each s integration extends over one unit cell, it leaves a contribution of only one μ-term from each sum (8) of δ-functions. Furthermore, since $P^{(3)}$ is periodic with respect to each s variable, one can drop any additive constants a_μ in the arguments. Making use now of (6), $n = 3$, and noting that the average density $\rho = n_v/v$, we obtain the following expression for $g^{(3)}$:

$$g^{(3)}(r_{12}, r_{13}, r_{23}) = \sum_{\nu_1 + \nu_2 + \nu_3 = 0} \exp\left(\sum_{i<j} W(r_{ij})b_{\nu_i} \cdot b_{\nu_j}\right)$$
$$\times \Gamma(b_{\nu_1})\Gamma(b_{\nu_2})\Gamma(b_{\nu_3})\langle\exp(i(b_{\nu_1} \cdot r_1 + b_{\nu_2} \cdot r_2 + b_{\nu_3} \cdot r_3))\rangle. \tag{10}$$

Here $\Gamma(b)$ is a 'unit-cell scattering amplitude' defined by

$$\Gamma(b) = \frac{1}{n_v} \sum_\sigma e^{-ib \cdot a_\sigma} \tag{11}$$

which also determines the coefficients C_ν in (1) by (see Baer 1979)

$$C_\nu = |\Gamma(b_\nu)|^2. \tag{11′}$$

In the simple case of one particle per unit cell, i.e. $n_v = 1$, we have

$$\Gamma(b) = 1. \tag{11″}$$

The angular brackets $\langle \, \rangle$ denote averaging over all orientations of the vectors r_1, r_2, r_3, rotated rigidly together while keeping L fixed in space, or alternatively averaging over all orientations of L, keeping the vectors r_1, r_2, r_3 fixed. Since the restriction on the summation in (10) implies

$$b_{\nu_3} = -(b_{\nu_1} + b_{\nu_2}) \tag{12}$$

the expression inside the angular brackets depends only on the relative position vectors $r_{13} = r_1 - r_3, r_{23} = r_2 - r_3$, making the expression independent of the frame of reference.

The reduction of the orientational averaging to a single quadrature is given in appendix A. Denoting by φ_{12} and ψ_{12} the angles between the pairs of vectors (r_{13}, r_{23}) and (b_{ν_1}, b_{ν_2}), respectively, we have by (A13)

$$\langle \exp(i(b_{\nu_1} \cdot r_{13} + b_{\nu_2} \cdot r_{23}))\rangle = 2 \int_0^{\pi/2} J_0(A \sin^2 \theta) J_0(B \cos^2 \theta) \sin \theta \cos \theta \, d\theta \qquad (13)$$

where $J_0(x)$ is the Bessel functions of order zero and

$$\left. \begin{array}{c} A \\ B \end{array} \right\} = (b_{\nu_1}^2 r_{13}^2 + b_{\nu_2}^2 r_{23}^2 + 2b_{\nu_1} b_{\nu_2} r_{13} r_{23}(\cos \varphi_{12} \cos \psi_{12} \pm \sin \varphi_{12} \sin \psi_{12}))^{1/2}. \qquad (14)$$

Although not apparent from this form, equation (13) must by definition, considering (12), be invariant to any permutation of the indices 1, 2, 3. In the special case when either $\varphi_{12} = 0$ or $\psi_{12} = 0$, $A = B$ and (13) reduces to (see Magnus *et al* 1966)

$$\langle \exp(i(b_{\nu_1} \cdot r_{13} + b_{\nu_2} \cdot r_{23}))\rangle = j_0(A) \qquad (15)$$

where $j_0(x) = (\sin x)/x$ is the spherical Bessel function of order zero.

It is instructive to examine the conditions for convergence of the sum in (10). Such conditions impose new restrictions on the function $W(r)$. In particular, convergence requires that when substituting (12) into (10) the quadratic form in b_{ν_1} and b_{ν_2}, on the RHS of (10), be negative definite. Thus, since we have

$$\sum_{1 \leqslant i < j \leqslant 3} W(r_{ij}) b_{\nu_i} \cdot b_{\nu_j} = -\sum_{i,j=1}^{2} Q_{ij} b_{\nu_i} \cdot b_{\nu_j} \qquad (16)$$

where

$$\begin{aligned} Q_{11} &= W(r_{13}) & Q_{22} &= W(r_{23}) \\ Q_{12} &= Q_{21} = \tfrac{1}{2}(W(r_{13}) + W(r_{23}) - W(r_{12})) \end{aligned} \qquad (17)$$

this requires that the determinant of the 2×2 matrix $\{Q_{ij}\}$ is positive. Denoting the determinant by Q, we have thus

$$4Q = 2W(r_{12})(W(r_{13}) + W(r_{23})) - (W(r_{12}))^2 - (W(r_{13}) - W(r_{23}))^2 > 0. \qquad (18)$$

This inequality holds when the $W(r_{ij})$ satisfy the triangle inequalities

$$W(r_{13}) + W(r_{23}) > W(r_{12}) \qquad |W(r_{13}) - W(r_{23})| < W(r_{12}). \qquad (19)$$

These inequalities hold indeed for the asymptotic form (4) of $W(r)$. Yet some triangle inequality might be violated for very short distances. Clearly $g(r_{12}, r_{23}, r_{13})$ must practically vanish for any pair distance smaller than a certain exclusion diameter, say r_0. By (1) this implies that $W(r) \simeq 0$ for $r \leqslant r_0$. Yet if this holds for one pair while (4) holds for the two other pairs, then (18) could still either hold or be violated, and correspondingly the double series in (10) would be either convergent or divergent. This indicates that certain modifications have to be made in (6) for very small pair distances.

4. Alternative representations of $g^{(3)}$

In correspondence with the aforementioned different representations of the theta functions, there are beside (10) alternative series representations for $g^{(3)}$, each converging more rapidly in a different domain of the pair distances r_{12}, r_{13}, r_{23}. Putting $r_{13} = r, r_{23} = s$ and $r_{12} = t$, we have now for the matrix elements Q_{ij} in (16)

$$\begin{aligned} Q_{11} &= W(r) & Q_{22} &= W(s) & Q_{12} &= Q_{21} = \tfrac{1}{2}W(r, s, t) \\ W(r, s, t) &\equiv W(r) + W(s) - W(t) \end{aligned} \qquad (17')$$

and for $g^{(3)}$ we have from (10)

$$g^{(3)}(r, s, t) = \sum_{\nu_1, \nu_2} \exp(-W(r)b_{\nu_1}^2 - W(s)b_{\nu_2}^2 - W(r, s, t)b_{\nu_1} \cdot b_{\nu_2})$$

$$\times \frac{1}{n_v^3} \sum_{\sigma_1, \sigma_2, \sigma_3} \exp(i(b_{\nu_1} \cdot a_{\sigma_{31}} + b_{\nu_2} \cdot a_{\sigma_{32}}))\langle \exp(i(b_{\nu_1} \cdot r + b_{\nu_2} \cdot s))\rangle$$

$$a_{\sigma_{31}} = a_{\sigma_3} - a_{\sigma_1} \qquad a_{\sigma_{32}} = a_{\sigma_3} - a_{\sigma_2}. \tag{20}$$

Noting (1) and (11′), the $\nu_1 = 0$ and $\nu_2 = 0$ terms can be summed to give (20) in the form

$$g^{(3)}(r, s, t) = 1 + (g(r) - 1) + (g(s) - 1) + \sum_{\nu_1, \nu_2 > 0}. \tag{20′}$$

Partial or full application of the Poisson sum formula to (20), to either the ν_1 or ν_2 summation or to the double summation, produces the following series representations of $g^{(3)}$:

(i) When applied to a single ν-summation, we obtain

$$g^{(3)}(r, s, t) = (4\pi W(r))^{-3/2} \sum_{\nu_2} e^{-(Q/W(r))b_{\nu_2}^2} \frac{1}{\rho} \sum_{\mu_1} \frac{1}{n_v^2} \sum_{\sigma_1, \sigma_2, \sigma_3} e^{ia_{\sigma_{32}} \cdot b_{\nu_2}}$$

$$\times \langle \exp\{-(4W(r))^{-1}[|a_{\mu_1 + \sigma_{31}} + r|^2$$

$$- iW(r, s, t)b_{\nu_2} \cdot (a_{\mu + \sigma_{31}} + r)]\} e^{is \cdot b_{\nu_2}}\rangle$$

$$a_{\mu_1 + \sigma_{31}} = a_{\mu_1} + a_{\sigma_{31}}. \tag{20-I}$$

In the multiple summation, μ_1 runs over the direct Bravais lattice points, ν_2 runs over the reciprocal-lattice points and the σs each run over the points within one unit cell. A second representation is obtained from (20-I) by interchanging r and s.

(ii) When applied to the double ν-summation, we obtain

$$g^{(3)}(r, s, t) = (4\pi Q^{1/2})^{-3} \frac{1}{\rho^2} \sum_{\mu_1, \mu_2} \frac{1}{n_v} \sum_{\sigma_1, \sigma_2, \sigma_3} \langle \exp\{-(4Q)^{-1}[W(s)|a_{\mu_1 + \sigma_{31}} + r|^2$$

$$+ W(r)|a_{\mu_2 + \sigma_{32}} + s|^2 - W(r, s, t)(a_{\mu_1 + \sigma_{31}} + r) \cdot (a_{\mu_2 + \sigma_{32}} + s)]\}\rangle \tag{20-II}$$

where Q is given by

$$4Q = 2W(t)(W(r) + W(s)) - (W(t))^2 - (W(r) - W(s))^2. \tag{18′}$$

The angular averages in (20) affect only those factors whose exponent is bilinear in position and lattice vectors. Hence, factoring out the orientation independent factors we can write the angular averages as

$$\langle \ \rangle_I = \exp[-(4W(r))^{-1}(u^2 + r^2 - iv \cdot u)]$$

$$\times \langle \exp[-(4W(r))^{-1}(2u - iv) \cdot r + ib_{\nu_2} \cdot s]\rangle \tag{21-I}$$

where

$$u = a_{\mu_1 + \sigma_{31}} \qquad v = W(r, s, t)b_{\nu_2}$$

and

$$\langle\rangle_{\mathrm{II}} = \exp\{-(4Q)^{-1}[W(s)(u_1^2 + r^2) + W(r)(u_2^2 + s^2) - W(r,s,t)(u_1 \cdot u_2 + r \cdot s)]\}$$
$$\times \langle\exp\{(4Q)^{-1}[(2W(s)u_1 - W(r,s,t)u_2) \cdot r$$
$$+ (2W(r)u_2 - W(r,s,t)u_1) \cdot s]\}\rangle \qquad (21\text{-}II)$$

where

$$u_1 = a_{\mu_1 + \sigma_{31}} \qquad u_2 = a_{\mu_2 + \sigma_{32}}.$$

The angular averages in (21-I) and (21-II) are given now by an expression analogous to (A13) where the Bessel functions depend on complex arguments and on pure imaginary arguments, respectively. In the latter case (A13) is rewritten as (A14).

5. Comment on effective pair potentials

A restrictive feature common to multi-Gaussian and multi-theta processes is the unique dependence of all higher-order distributions on the pair distribution. This is indeed the case for systems with only pairwise molecular interactions, but in principle it is incorrect for systems with triplet and higher-order interaction potentials. Yet given expressions for g and $g^{(3)}$, we can obtain an effective pair potential $u(r)$ by solving the following equation from the BBGKY hierarchy:

$$\nabla_1 g(r_{12}) + g(r_{12})\nabla_1 \beta u(r_{12})$$
$$= -\rho \int \nabla_1 \beta u(r_{13})(g^{(3)}(r_{12}, r_{13}, r_{23}) - g(r_{12})g(r_{13})) \, \mathrm{d}^3 r_3. \qquad (22)$$

Putting in (22) $r_{12} = r$, $r_{13} = s$, $r_{23} = t$ and introducing

$$\psi(r) = \beta u'(r) \qquad (23)$$

and the weighted average of $g^{(3)}$

$$\bar{h}(r, s) = 2 \int_0^\pi g^{(3)}(r, s, t) \cos\varphi \sin\varphi \, \mathrm{d}\varphi \qquad \text{where } \cos\varphi = (r^2 + s^2 - t^2)/2rs$$
$$(24)$$

we can rewrite (22) in the form

$$g(r)\psi(r) + g'(r) = -\pi\rho \int_0^\infty s^2 \psi(s)\bar{h}(r, s) \, \mathrm{d}s. \qquad (25)$$

This is a linear integral equation in $\psi(r)$. Note that $g'(r)$ is available in closed form from a term-by-term analytic differentiation of (1), but $\bar{h}(r, s)$ has to be obtained by numerical integration of (20) substituted into (24). Equation (25) can be solved by reducing it to an algebraic equation on a finite grid of points r_i (see Haymet and Rice 1982). The pair potential is then obtained from

$$\beta u(r) = -\int_r^\infty \psi(s) \, \mathrm{d}s \qquad (26)$$

evaluated numerically by replacing the integral by partial sums over the grid.

One should keep in mind that in practice even a slight change in the chosen local lattice could account for the difference between systems having practically the same pair

distribution but differing significantly by their triplet or higher interaction potentials and by their corresponding molecular distributions.

Necessarily, if we make use only of scattering data at a single thermodynamic state, we cannot expect to find with the present procedure anything beyond an effective pair potential. However, given scattering data for several states, say for several temperatures along an isochore or an isobar, we may expect to find some hints about the more detailed nature of the molecular interactions, say through the persistence of a certain parent local L over the range of temperatures.

It has been occasionally stated that a small difference in the triplet potentials could be responsible for crystallization into a preferred crystal lattice (see e.g. Jansen 1965). By the same toke a delicate balance between many-body interactions could be responsible for such a preferred crystallization (see e.g. Niebel and Venables 1974). Since we know little about such overall many-body effects, it would seem reasonable to give a microscopic description of the condensed system in terms of local structures L and the extent of their spatial coherence, which are characteristic of the overall molecular interactions and determine uniquely an effective pair potential, rather than in terms of a truncated hierarchy of potentials producing marginal and inconclusive results concerning preferred lattice structures.

Appendix

We will calculate the orientational average:

$$\Omega = \langle e^{i(k_1 \cdot r_1 + k_2 \cdot r_2)} \rangle. \tag{A1}$$

The following two triangles, $\mathcal{H}$ and $\mathcal{K}$, arbitrarily oriented in space, are each defined by a pair of vectors and the angle between them:

$$\mathcal{H} = (r_1, r_2, \varphi) \qquad \mathcal{K} = (k_1, k_2, \psi). \tag{A2}$$

Let $\mathcal{K}$ define a fixed coordinate system such that $\mathcal{K}$ lies in the xy plane with k_1 directed along the positive x axis and k_2 has a positive y component. Now let $\mathcal{H}$ be rotated rigidly to a new position such that the rotated triangle $\mathcal{H}^0 = (r_1^0, r_2^0, \varphi)$ lies in the plane of $\mathcal{K}$ with r_1^0 directed along the positive x axis, i.e. parallel to k_1, and r_2^0 has a positive y component. Using a representation of vectors in spherical harmonics components, i.e. $a = (a_m, m = -1, 0, 1)$, we have in particular for a unit vector $e^0(\omega)$ lying in the xy plane and making an angle ω with x axis:

$$e^0(\omega) = \begin{bmatrix} (1/\sqrt{2}) \, e^{-i\omega} \\ 0 \\ (1/\sqrt{2}) \, e^{i\omega} \end{bmatrix} \tag{A3}$$

and hence we have

$$k_1 = k_1 e^0(0) \qquad k_2 = k_2 e^0(\psi) \qquad r_1^0 = r_1 e^0(0) \qquad r_2^0 = r_2 e^0(\varphi). \tag{A4}$$

Furthermore, let the rotation taking $\mathcal{H}^0$ into $\mathcal{H}$, defined in terms of Eulerian angles, be denoted by $\mathcal{R} = \mathcal{R}(\alpha, \beta, \gamma)$, with the corresponding transformation matrix $\mathcal{D}(\mathcal{R}) = \mathcal{D}(\alpha, \beta, \gamma)$ belonging to the $l = 1$ representation of the rotation group (see e.g. Tinkham 1964). We obtain then the following representation for the transformed unit vector:

$$e(\omega) = \mathcal{R}e^0(\omega) = \begin{bmatrix} (1/\sqrt{2}) \, e^{-i\alpha} [\frac{1}{2}(1 + \cos \beta) \, e^{-i(\gamma + \omega)} + \frac{1}{2}(1 - \cos \beta) \, e^{i(\gamma + \omega)}] \\ (1/\sqrt{2}) \, \frac{1}{2}\sin \beta (e^{-i(\gamma + \omega)} + e^{i(\gamma + \omega)}) \\ (1/\sqrt{2}) \, e^{i\alpha} [\frac{1}{2}(1 - \cos \beta) \, e^{-i(\gamma + \omega)} + \frac{1}{2}(1 + \cos \beta) \, e^{i(\gamma + \omega)}] \end{bmatrix}. \tag{A5}$$

Noting that a scalar product is given in spherical harmonic components by

$$\boldsymbol{a} \cdot \boldsymbol{b} = \sum_m a_m^* b_m \tag{A6}$$

we substitute (A5) with (A4) into (A1) and obtain the orientational average in the form

$$\Omega = \frac{1}{8\pi^2} \int \int \int \exp[i(F(u) + G(v))] \, d\alpha \, d\gamma \, d\cos\beta \tag{A7}$$

where

$$
\begin{aligned}
F(u) &= \tfrac{1}{2}(1 - \cos\beta)(k_1 r_1 \cos u + k_2 r_2 \cos(u - \sigma)) \\
G(v) &= \tfrac{1}{2}(1 + \cos\beta)(k_1 r_1 \cos v + k_2 r_2 \cos(v + \delta))
\end{aligned}
\tag{A8}
$$

with

$$u = \alpha - \gamma \qquad v = \alpha + \gamma \qquad \delta = \varphi - \psi \qquad \sigma = \varphi + \psi. \tag{A9}$$

Since $d\alpha \, d\gamma = \tfrac{1}{2} du \, dv$ and the integrand in (A7) is doubly periodic both in (α, γ) and in (u, v), we can replace the averaging over the rectangle $-\pi \le \alpha, \gamma \le \pi$ by an averaging over the rectangle $-\pi \le u, v \le \pi$. Furthermore, since we can rewrite (A8) as

$$F(u) = \tfrac{1}{2}(1 - \cos\beta)A \cos(u + p) \qquad G(v) = \tfrac{1}{2}(1 + \cos\beta)B \cos(v + q) \tag{A10}$$

where

$$
\begin{aligned}
A &= (k_1^2 r_1^2 + k_2^2 r_2^2 + 2 k_1 k_2 r_1 r_2 \cos\sigma)^{1/2} \\
B &= (k_1^2 r_1^2 + k_2^2 r_2^2 + 2 k_1 k_2 r_1 r_2 \cos\delta)^{1/2}
\end{aligned}
\tag{A11}
$$

(A7) can be written as

$$\Omega = \frac{1}{2} \int_{-1}^{1} d\cos\beta \, \frac{1}{\pi} \int_0^\pi \exp(i \sin^2(\beta/2) A \cos u) \, du \, \frac{1}{\pi} \int_0^\pi \exp(i \cos^2(\beta/2) B \cos v) \, dv \tag{A12}$$

resulting in (see e.g. Magnus *et al* 1966)

$$\Omega = 2 \int_0^{\pi/2} J_0(A \sin^2 \theta) J_0(B \cos^2 \theta) \sin\theta \cos\theta \, d\theta \tag{A13}$$

where $J_0(x)$ is the Bessel function of order zero.

If we replace k_1 and k_2 in (A1) by the imaginary vectors $-i k_1$ and $-i k_2$, then A and B become pure imaginary, or alternatively keeping definition (A11), we can now write (A13) in terms of the modified Bessel functions:

$$\Omega' = \langle \exp(k_1 \cdot r_1 + k_2 \cdot r_2) \rangle = 2 \int_0^{\pi/2} I_0(A \sin^2 \theta) I_0(B \cos^2 \theta) \sin\theta \cos\theta \, d\theta. \tag{A13$'$}$$

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