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SYMMETRY, LANDAU THEORY AND POLYTOPE MODELS OF GLASS

David R. NELSON and Michael WIDOM

Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA

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Order in supercooled liquids and metallic glasses is related to a regular icosahedral "crystal" consisting of 120 particles inscribed on the surface of a sphere in four dimensions. Hyperspherical harmonics and the discrete symmetry group of this four-dimensional platonic solid can be used to construct an order parameter for glasses in three-dimensional flat space. A uniformly frustrated Landau expansion in this order parameter suggests a ground state with a regular array of wedge disclination lines. Homotopy theory is used to classify all topologically stable defects. A generalization of Bloch's theorem for electronic states in flat space solids allows explicit diagonalization of tight binding models defined on the curved-space icosahedral crystal.

1. Introduction

As pointed out many years ago by Frank [1], most simple pair potentials lead to a strong energetic preference for twelve-particle icosahedral coordination shells surrounding atoms in dense liquids. *Correlations* in the orientations of neighboring icosahedra which increase with decreasing temperatures have been observed in recent molecular dynamics simulations of supercooled liquids [2]; similar correlations [2] appear in simple models of metallic glass [3, 4]. Frustration prevents long-range icosahedral order however, and forces a finite density of defects into the ground state*. The incompatibility of local icosahedral order with a space-filling icosahedral "crystal" seems to be the key to understanding the structure and statistical mechanics of simple glass-formers.

As described in detail by Coxeter [5, 6], particles with icosahedral coordination shells *do* tile the surface of a sphere in four dimensions, forming a four-dimensional platonic solid, or "polytope". Following Schlafli [5, 6], we shall call this 120-vertex object "polytope $\{3, 3, 5\}$", to emphasize that it is composed of tetrahedral cells of four particles (denoted $\{3, 3\}$), with 5 tetrahedra per near-neighbor bond. In an interesting early paper [7] Coxeter suggested that dense random packing models (now commonly used to describe metallic glasses [3, 4]) could be approximated by a fictitious space-filling "statistical honeycomb" polytope $\{3, 3, q\}$, with a fractional

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* By "frustration", we mean that all atoms cannot simultaneously sit in the minima presented to them by the pair potentials of their near neighbors. A closely related kind of frustration appears in uniformly frustrated spin glasses.

number q of tetrahedra per bond. The simplest such model has $q = 2\pi/\cos^{-1}\frac{1}{3} \doteq 5.104$ [5]. Today, we would call this an "effective medium" or "mean field" approach.

It is more realistic to imagine a predominantly icosahedral medium interrupted occasionally by defects. As pointed out by Kléman and Sadoc [8], defects such as disclinations are necessary to flatten curved space polytopes. The importance of the polytope $\{3, 3, 5\}$ for metallic glasses (and for covalently bonded glasses like SiO_2) has been emphasized by Sadoc [9] and by Sadoc and Mosseri [10]. Numerical calculations of defect-free tight binding models of electronic states defined on $\{3, 3, 5\}$ seem to give reasonable agreement with densities of states for flat-space amorphous semiconductors [11]. Recently [12], the defects which frustrate icosahedral order in flat space have been characterized more precisely using homotopy theory and the icosahedral orientational order parameter defined in ref. [2]. The curvature mismatch between flat space and the curved space polytope $\{3, 3, 5\}$ forces an asymmetry in the density of +72° and −72° wedge disclination lines. Microscopically, these lines correspond respectively to contiguous links of "anomalous" bonds surrounded by four and six tetrahedra. The Frank–Kasper phases of complex transition-metal alloys [13] are an interesting example of ordered arrays of frustration-induced −72° disclination lines; the *average* number of tetrahedra per bond $\bar{q}$ is quite close to the value $2\pi/\cos^{-1}\frac{1}{3}$ discussed by Coxeter [5]. The defect lines are characterized by non-abelian SU(2) matrix charges, which leads to entanglement as they attempt to form an ordered network when cooled rapidly [12]. A tangled array of −72° disclination lines in an otherwise icosahedral medium is an appealing model for a metallic glass. Sethna [14] has recently suggested a uniformly frustrated continuum elastic free energy to describe this situation.

The set of symmetry operations G of the polytope $\{3, 3, 5\}$ which are proper rotations form a 7200 element discrete subgroup of SO(4) [15]. In this paper, we exploit this symmetry group in three different ways. The first concerns the coefficients Q_{12,m_1m_2} in an expansion in hyperspherical harmonics [16] applied to 120 particles in S^3 (the surface of a sphere in four dimensions). The subscript $n = 0, 1, \ldots$ indexes irreducible representations of SO(4), and the indices m_1 and m_2 run in integral steps from $-\frac{1}{2}n$ to $\frac{1}{2}n$. The symmetry group G greatly restricts the allowed spherical harmonics in the configuration $\{3, 3, 5\}$, which is presumably the ground state for particles interacting via simple pair potentials. The first nontrivial spherical harmonics occur for $n = 12$. As will be discussed in detail in sects. 2 and 3, the allowed values of the index n are related to the concept of reciprocal lattice vectors in flat space solids. This description of particles in S^3 leads quite naturally to an order parameter for glasses in flat space via stereographic projection of a local particle configuration into S^3. A related construction is used in Sethna's continuum elastic theory [14]. Both translational and orientational icosahedral symmetries are embodied in this order parameter, in contrast to the purely orientational symmetries studied in ref. [2]. A Landau expansion in position-dependent "Fourier" coefficients

$Q_{12,m_1m_2}(\boldsymbol{r})$ turns out to be reminiscent of Landau theories for the blue phases of choelesteric liquid crystals, which are ordered arrays of disclination lines in a chiral nematic [17–19]. The generators of the $n = 12$ representation of SO(4) are used to produce a uniformly frustrated covariant derivative. At low temperatures, we recover Sethna's continuum elastic free energy, except that his 4×4 SO(4) matrices are replaced by 169-dimensional $n = 12$ SO(4) representation matrices. Both theories depend only on the six SO(4) "Euler angles" at low temperatures.

We also use the symmetry group G to discuss line defects in glasses, which are described by the homotopy classes [20] of $\pi_1(\mathrm{SO(4)/G})$. Only the subgroup of disclination defects was studied in ref. [12]. Here, we show that the complete defect classification is given by

$$\pi_1(\mathrm{SO}(4)/\mathrm{G}) = \mathrm{Y}' \times \mathrm{Y}' , \tag{1.1}$$

where Y′ is the 120-element lift of the icosahedral point group Y into SU(2). The diagonal elements in this direct product are the disclinations studied in ref. [12]; these include the wedge disclinations forced into the medium by the curvature mismatch of flat space with the polytope {3, 3, 5}.

As a final application of the symmetry group G, we show how to explicitly diagonalize tight-binding models defined on {3, 3, 5}. The simplest such model is described by the hamiltonian

$$H = -t \sum_{\langle i,j\rangle} (|i\rangle\langle j| + |j\rangle\langle i|) , \tag{1.2}$$

where t is a hopping matrix element connecting nearest-neighbor sites on the polytope, and $\{|i\rangle\}$ is a set of orthonormal basis functions localized at the sites $\{i\}$. These basis functions generate a 120-element reducible representation of the group G. Here, we exploit the relationship [15]

$$\mathrm{G} = (\mathrm{Y}' \times \mathrm{Y}')/\mathrm{Z}_2 \tag{1.3}$$

to show that this representation breaks into nine irreducible representations [21] (α, α) indexed by the irreducible representations α of Y′. The dimensionalities of these representations (which give the degeneracies of the 120 eigenvalues of H) are summarized by the formula

$$120 = 1 \oplus 4 \oplus 4 \oplus 9 \oplus 9 \oplus 16 \oplus 16 \oplus 25 \oplus 36 . \tag{1.4}$$

As discussed in sect. 5, the eigenvalues for arbitrary rotationally invariant tight binding models with one level per site have a very simple analytic expression in terms of the character table of Y′.

In sect. 2, we show how to analyze particle configurations on a sphere using hyperspherical harmonics. The Landau description of a glass is developed in sect.

3. We summarize the properties of the homotopy group $\pi_1(\mathrm{SO}(4)/\mathrm{G})$ in sect. 4, and turn to a discussion of tight binding models in sect. 5.

2. Icosahedral order parameter

2.1. STRUCTURE FUNCTIONS IN S^3

Crystalline order in euclidean space shows up most clearly in the structure function, a quantity directly accessible to experiment via X-ray diffraction. Before describing an analogous object for particles confined to the surface of a four-dimensional sphere, we briefly recall the salient ideas in flat space [22]. Because of the periodicity embodied in a crystalline lattice, it is natural to expand the particle density in a Fourier series

$$\rho(\boldsymbol{r}) = \sum_{\boldsymbol{q}} \rho_{\boldsymbol{q}}\, \mathrm{e}^{-i\boldsymbol{q}\cdot\boldsymbol{r}}, \tag{2.1}$$

where the Fourier coefficients $\rho_{\boldsymbol{q}}$ are given by

$$\rho_{\boldsymbol{q}} = \frac{1}{V}\int \mathrm{d}^3 r\, \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}} \rho(\boldsymbol{r}) . \tag{2.2}$$

The integral in (2.2) is over a volume V, and the precise $\boldsymbol{q}$-values entering (2.1) are restricted by, say, periodic boundary conditions. These $\boldsymbol{q}$'s, of course, close up to form a continuum in the limit of an infinite system. Nonzero Fourier coefficients are possible for any $\boldsymbol{q}$ in a liquid. In a classical crystal at $T=0$, however, $\rho_{\boldsymbol{q}}$ is nonzero only for a discrete set of reciprocal lattice vectors $\{\boldsymbol{G}\}$. The collection of Fourier coefficients $\{\rho_{\boldsymbol{G}}\}$ constitute a set of order parameters for a crystalline solid. Landau [23] has used the $\rho_{\boldsymbol{G}}$'s with the smallest nonzero reciprocal lattice vectors to construct an order parameter theory of freezing.

X-ray diffraction experiments on liquids and solids measure the structure function

$$\mathcal{S}(\boldsymbol{q}) = \langle |\rho_{\boldsymbol{q}}|^2 \rangle , \tag{2.3}$$

where the brackets denote a thermal expectation value. In practice, one is usually forced to work with samples composed of randomly oriented microcrystallites, and measures instead of the angular or "powder" average of eq. (2.3)

$$S(q) = \frac{1}{4\pi}\int \mathrm{d}\Omega_{\boldsymbol{q}} \mathcal{S}(\boldsymbol{q}) . \tag{2.4}$$

Here, $\mathrm{d}\Omega_{\boldsymbol{q}}$ is an element of solid angle in q-space. Standard manipulations using (2.2)–(2.4) suffice to show that $S(q)$ is related to a radially averaged correlation function $G(r)$ by [24]

$$S(q) = \frac{4\pi}{V}\int_0^{\infty} r^2\, \mathrm{d}r \frac{\sin(qr)}{qr} G(r) . \tag{2.5}$$

This radial correlation function is an angular average in real space of the density–density correlation function,

$$G(r)=\frac{1}{4\pi}\int \mathrm{d}\Omega_r\,\langle\rho(\boldsymbol{r})\rho(\boldsymbol{0})\rangle\,. \tag{2.6}$$

The structure function $S(q)$ in a solid has peaks when $q=|\boldsymbol{G}|$, where $\boldsymbol{G}$ is a reciprocal lattice vector. It is this powder-averaged structure function, rather than $\mathscr{S}(\boldsymbol{q})$, which has a simple analogue in S^3.

Consider a collection of particles on the surface of a four-dimensional sphere with unit radius. Denoting a position on this sphere by a unit four-vector $\hat{\boldsymbol{u}}$, we expand the particle density $\rho(\hat{\boldsymbol{u}})$ in hyperspherical harmonics $Y_{n,m_1m_2}(\hat{\boldsymbol{u}})$

$$\rho(\hat{\boldsymbol{u}})=\sum_{n,m_1,m_2} Q_{n,m_1m_2}Y^*_{n,m_1m_2}(\hat{\boldsymbol{u}})\,. \tag{2.7}$$

The hyperspherical harmonics $Y_{n,m_1m_2}(\hat{\boldsymbol{u}})$ are a particularly convenient complete set of functions on S^3. As described in detail in ref. [16], the $Y_{n,m_1m_2}(\hat{\boldsymbol{u}})$ are proportional to the Wigner matrices of the $l=\frac{1}{2}n$ representation of SU(2)

$$Y_{n,m_1m_2}(\hat{\boldsymbol{u}})=\sqrt{\frac{n+1}{2\pi^2}}\,D^{n/2}_{m_1m_2}(\alpha,\beta,\gamma)\,. \tag{2.8}$$

The Euler angles α, β and γ which appear in (2.8) are obtained from $\hat{u}$ using the well-known isomorphism between the elements of SU(2) and points on a four-dimensional sphere [16, 21]. Upon writing $\hat{\boldsymbol{u}}=(u_0, u_x, u_y, u_z)$, and setting

$$a=u_0+iu_z\,,\quad b=iu_x+u_y\,, \tag{2.9}$$

we have [21]

$$D^l_{mm'}(\hat{\boldsymbol{u}})=\sum_{\mu}\frac{[(l+m)!(l-m)!(l+m')!(l-m')!]^{1/2}}{(l+m-\mu)!\,\mu!\,(l-m'-\mu)!\,(m'-m+\mu)!}\times a^{l+m-\mu}(a^*)^{l-m'-\mu}b^{\mu}(-b^*)^{m'-m+\mu}\,. \tag{2.10}$$

This sum over integers μ is made finite by the factorials in the denominator. The identification of the four-dimensional hyperspherical harmonics $Y_{n,m_1m_2}(u)$ (which are basis functions for a set of irreducible representations of SO(4)) with the representation *matrices* of SU(2) is a remarkable and very useful coincidence. This coincidence makes it clear that for every $n=0, 1, \ldots,$ we have $(n+1)^2$ independent basis functions, obtained by varying m_1 and m_2 from $-\frac{1}{2}n$ to $\frac{1}{2}n$ in integral steps.

Eq. (2.7) is readily inverted to obtain the Fourier coefficients Q_{n,m_1m_2}. Using the orthogonality relation [16]

$$\int \mathrm{d}\Omega_{\hat{u}}\;Y_{n,m_1m_2}(\hat{\boldsymbol{u}})Y^*_{n',m_1'm_2'}(\hat{\boldsymbol{u}})=\delta_{nn'}\delta_{m_1m_1'}\delta_{m_2m_2'}\,, \tag{2.11}$$

we find that

$$Q_{n,m_1m_2}=\int \mathrm{d}\Omega_{\hat{u}}\; Y_{n,m_1m_2}(\hat{\boldsymbol{u}})\rho(\hat{\boldsymbol{u}})\,. \tag{2.12a}$$

The integral over S^3 in eq. (2.12a) can be carried out using polar coordinates

$$\hat{\boldsymbol{u}}=(\cos\psi, \sin\psi\sin\theta\cos\phi, \sin\psi\sin\theta\sin\phi, \sin\psi\cos\theta) \tag{2.12b}$$

and the integration measure

$$\int \mathrm{d}\Omega_{\hat{u}}=\int_0^{\pi}\sin^2\psi\,\mathrm{d}\psi\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi\,. \tag{2.12c}$$

In analogy with eq. (2.3), we define a thermally averaged structure function

$$\mathcal{S}_{n,m_1m_2}\equiv\langle|Q_{n,m_1m_2}|^2\rangle\,. \tag{2.13}$$

The Q_{n,m_1m_2} transform like a $(n+1)^2$-dimensional representation of SO(4). When we rotate the external coordinate system which defines $\hat{\boldsymbol{u}}$, the $(n+1)^2$ numbers Q_{n,m_1m_2} for a particular n are scrambled. It is easily shown, however, that

$$S_n\equiv\frac{1}{(n+1)^2}\sum_{m_1m_2}\mathcal{S}_{n,m_1m_2} \tag{2.14}$$

is rotationally invariant. The quantity S_n is the analogue of the powder-averaged X-ray structure function. To see this in more detail, we substitute eqs. (2.12a) and (2.13) into (2.14) and use the identity [16]

$$\sum_{m_1m_2}Y_{n,m_1m_2}(\hat{\boldsymbol{u}}_a)Y^*_{n,m_1m_2}(\hat{\boldsymbol{u}}_b)=\frac{n+1}{2\pi^2}\,\frac{\sin[(n+1)\psi]}{\sin\psi}\,, \tag{2.15}$$

where ψ is the angle between the four-vectors $\hat{\boldsymbol{u}}_a$ and $\hat{\boldsymbol{u}}_b$. It follows that

$$S_n=\frac{1}{2\pi^2(n+1)}\int\mathrm{d}\Omega_a\int\mathrm{d}\Omega_b\frac{\sin[(n+1)\psi]}{\sin\psi}\langle\rho(\hat{\boldsymbol{u}}_a)\rho(\hat{\boldsymbol{u}}_b)\rangle\,. \tag{2.16}$$

We now change variables in eq. (2.16), letting

$$\int\mathrm{d}\Omega_a\int\mathrm{d}\Omega_b\to\int\mathrm{d}\Omega_R\int\mathrm{d}\Omega_b\,, \tag{2.17}$$

where R is an element of SO(4) which rotates $\hat{\boldsymbol{u}}_b$ into $\hat{\boldsymbol{u}}_a$. The sets of physically distinct elements R which rotate $\hat{\boldsymbol{u}}_b$ into $\hat{\boldsymbol{u}}_a$ constitutes the coset space SO(4)/SO(3). This in turn is isomorphic to S^3, so we can parametrize the integration measure $\mathrm{d}\Omega_R$ as in eq. (2.12c) with polar angles. Note that ψ is the angle between $\hat{\boldsymbol{u}}_a$ and $\hat{\boldsymbol{u}}_b$. We shall also use the fact that, in thermal equilibrium, we have

$$\langle\rho(\hat{\boldsymbol{u}}_a)\rho(\hat{\boldsymbol{u}}_b)\rangle=\langle\rho(R\hat{\boldsymbol{u}}_b)\rho(\hat{\boldsymbol{u}}_b)\rangle=\langle\rho(R\mathbf{1})\rho(\mathbf{1})\rangle\,. \tag{2.18}$$

Since the average in eq. (2.18) includes configurations related by a rigid SO(4) rotation, we have, without loss of generality, replaced the point $\hat{\boldsymbol{u}}_b$ by $\mathbf{1}\equiv(1,0,0,0)$.

Upon defining the "radially" averaged correlation function

$$G(\psi)=\frac{1}{4\pi}\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi\,\langle\rho(R1)\rho(1)\rangle\,, \tag{2.19}$$

we obtain finally

$$S_n=\frac{4\pi}{n+1}\int_0^{\pi}\sin^2\psi\,\mathrm{d}\psi\frac{\sin[(n+1)\psi]}{\sin\psi}G(\psi)\,, \tag{2.20}$$

in close analogy with eq. (2.5). To take the flat space limit of eq. (2.20), we set $\psi=\kappa r$, where r is a geodesic distance on S^3 and κ is the inverse radius of the sphere. We note in addition that the correlation function G must in general be a function of r only for spheres which are not of unit radius. Taking the limit $\kappa\to 0$ and $n\to\infty$ in such a way that $n\kappa\equiv q$ remains fixed, we find that

$$S_n\to\frac{8\pi^3}{V}\int_0^{\infty}r^2\,\mathrm{d}r\frac{\sin(qr)}{qr}G(r)=2\pi^2S(q)\,, \tag{2.21}$$

where $V=2\pi^2\kappa^{-3}$ is the area of the four-dimensional sphere. Thus, S_n becomes proportional to $S(q)$ in the flat space limit.

In analogy with the Bragg peaks expected in $S(q)$ for flat space crystals, we expect that S_n will be nonzero only for a discrete subset of n's for 120 particles arranged in the configuration $\{3,3,5\}$. The allowed n's will be determined in subsect. 2.3. First, however, we summarize the remarkable properties of the symmetry group G of polytope $\{3,3,5\}$.

2.2. SYMMETRIES OF {3, 3, 5}

Fig. 1 shows a projection [6] of the 120 vertices and 720 near-neighbor bonds of the polytope $\{3,3,5\}$. To efficiently deal with symmetries of this object we need a concise way to enumerate the vertices and bonds. An especially useful enumeration exploits the isomorphism [15, 16] between points on the four-dimensional sphere S^3 and the group SU(2). A point $\hat{\boldsymbol{u}}\in S^3$ can be thought of as a unit four-vector with components

$$\hat{\boldsymbol{u}}=(\cos\psi,\,n_x\sin\psi,\,n_y\sin\psi,\,n_z\sin\psi)\,, \tag{2.22}$$

where $\hat{\boldsymbol{n}}=(n_x,n_y,n_z)\in S^2$ is a unit three-vector. Alternatively we can write $\hat{\boldsymbol{u}}$ as an SU(2) matrix u through the identification

$$\hat{\boldsymbol{u}}\to u\equiv 1\cos\psi+i\hat{\boldsymbol{n}}\cdot\boldsymbol{\sigma}\sin\psi\,, \tag{2.23}$$

where 1 is the 2×2 unit matrix and the σ_i are Pauli matrices.

Two points u, $v\in S^3$ can now be multiplied together by using the multiplication rules of Pauli matrices. The sphere S^3 has now been given the algebraic structure of the group SU(2). Henceforth we shall regard points in S^3 as synonomous with

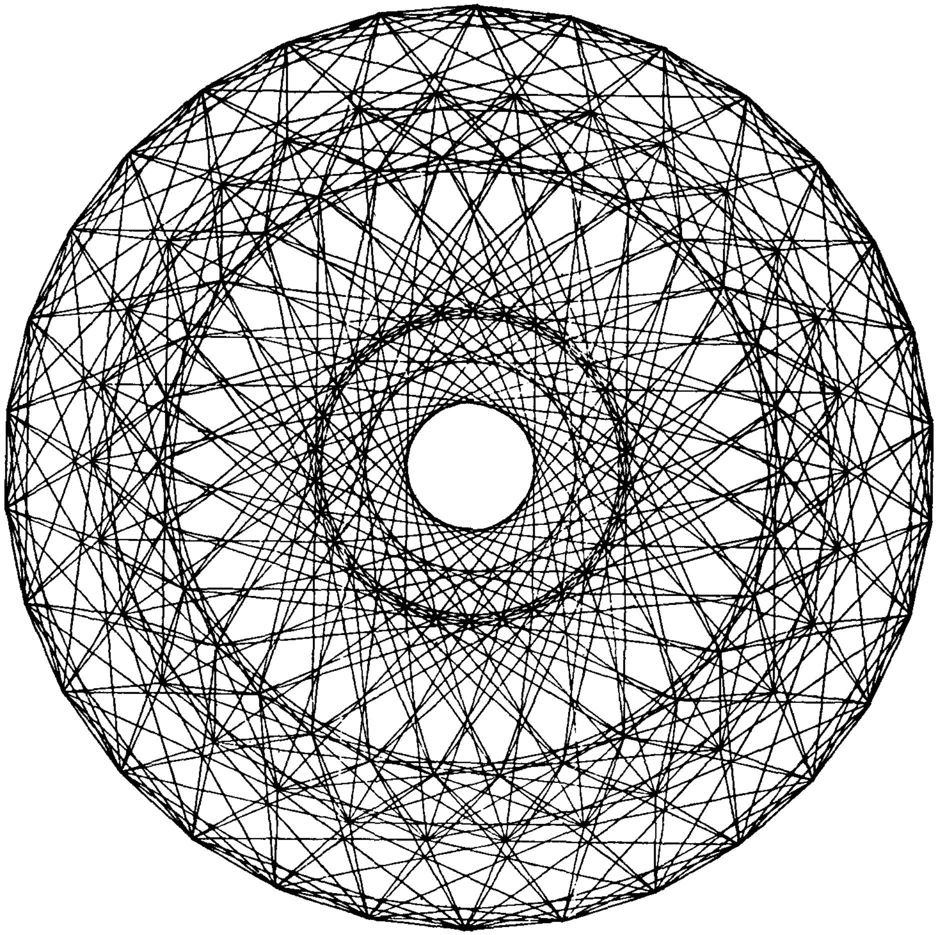

Fig. 1. Polytope {3, 3, 5}, from ref. [6].

SU(2) matrices. As demonstrated in the book by Du Val [15], the vertices of {3, 3, 5} can be identified with the lift into SU(2) of the 60-element icosahedral point group Y. The 120-element group Y′ which results describes, among other things, the algebra of disclination line defects in a glass [12]. Because of its importance we shall summarize the properties of Y′ which will be used in this paper.

The two-element lift of an SO(3) rotation $R_{\hat{n}}(\theta)$ into SU(2) is given by the pair of matrices $\pm e^{\frac{1}{2}i(\hat{n}\cdot\boldsymbol{\sigma})\theta}$. The symmetry group Y of an icosahedron contains five conjugacy classes. The group Y′ which is the lift of Y into SU(2) contains nine conjugacy classes. The identity in Y lifts to the classes

$$C_0 = 1\,, \tag{2.24a}$$

$$\bar{C}_0 = -1\,. \tag{2.24b}$$

The twenty rotations by ±2$\pi/3$ lift to the classes

$$C_3 = \{e^{\frac{1}{2}i(\hat{n}\cdot\sigma)2\pi/3}\colon\ \hat{n}\text{ points to faces of icosahedron}\}\,, \tag{2.25a}$$

$$\bar{C}_3 = \{-u\colon\ u \in C_3\}\,. \tag{2.25b}$$

The twelve rotations by ±2$\pi/5$ lift to the classes

$$C_5 = \{e^{\frac{1}{2}i(\hat{n}\cdot\sigma)2\pi/5}\colon\ \hat{n}\text{ points to vertices of icosahedron}\}\,, \tag{2.26a}$$

$$\bar{C}_5 = \{-u\colon\ u \in C_5\}\,. \tag{2.26b}$$

The twelve rotations by ±4$\pi/5$ lift to the classes

$$C_5^2 = \{u^2\colon\ u \in C_5\}\,, \tag{2.27a}$$

$$\overline{C_5^2} = \{-u^2\colon\ u \in C_5\}\,. \tag{2.27b}$$

Finally, the fifteen rotations by π lift to the class

$$C_2 = \{e^{\frac{1}{2}i(\hat{n}\cdot\sigma)\pi}\colon\ \hat{n}\text{ points to edges of icosahedron}\}\,. \tag{2.28}$$

The character table for Y′ is displayed in table 1. Because Y′ is a subgroup of SU(2), we guessed that some of its irreducible representations would be generated by the lth irreducible representation functions of SU(2), with $l = 0, \frac{1}{2}, 1, \ldots$. The irreducible representations A, E_1, F_1, G_1, H and I were obtained in this way. The dimensions of the remaining irreducible representations are constrained by the sum rule

$$\sum_{\alpha} d_{\alpha}^2 = 120\,, \tag{2.29}$$

where d_α is the dimension of the representation α. The remainder of the character table follows from requiring orthogonality of its rows and columns.

This character table will prove useful in sect. 5, when we discuss the eigenvalues of tight binding models defined on {3, 3, 5}. As an additional application, we now

TABLE 1

Character table of Y′: $\tau = \frac{1}{2}(\sqrt{5}+1)$

Y′	$1C_0$	$1\bar{C}_0$	$30C_2$	$20C_3$	$20\bar{C}_3$	$12C_5$	$12\bar{C}_5$	$12C_5^2$	$12\bar{C}_5^2$
A	1	1	1	1	1	1	1	1	1
E_1	2	−2	0	1	−1	τ	$-\tau$	τ^{-1}	$-\tau^{-1}$
E_2	2	−2	0	1	−1	$-\tau^{-1}$	τ^{-1}	$-\tau$	τ
F_1	3	3	−1	0	0	τ	τ	$-\tau^{-1}$	$-\tau^{-1}$
F_2	3	3	−1	0	0	$-\tau^{-1}$	$-\tau^{-1}$	τ	τ
G_1	4	−4	0	−1	1	1	−1	−1	1
G_2	4	4	0	1	1	−1	−1	−1	−1
H	5	5	1	−1	−1	0	0	0	0
I	6	−6	0	0	0	−1	1	1	−1

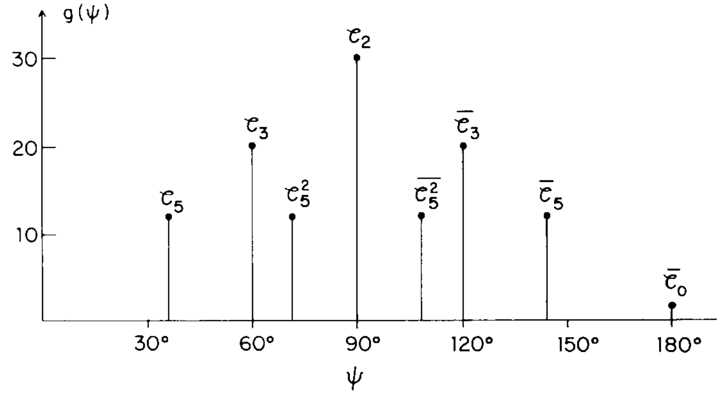

Fig. 2. Radial distribution function of polytope {3, 3, 5}. Peaks are labelled by classes of Y′ (see table 1).

show that it determines the radial distribution $g(\psi)$ of {3, 3, 5} (see fig. 2). The function $g(\psi)$ gives the number of points at geodesic distance ψ from a reference point, which we take to be

$$1 \equiv \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} . \tag{2.30}$$

This radial distribution function has been discussed in the context of metallic glasses by Sadoc [9], and is closely related to the radially averaged correlation function $G(\psi)$ discussed in sect. 2.1. If S^3 is of unit radius, ψ is just the angle between 1 and the point under consideration. It is straightforward to show that the angle between two arbitrary points $u, v \in S^3$ is

$$\psi(u, v) = \cos^{-1}\left(\tfrac{1}{2}\,\mathrm{Tr}\,\{uv^{\dagger}\}\right) , \tag{2.31}$$

where the dagger denotes a hermitian conjugate, $v^{\dagger} = v^{-1}$. The distance between $u \in S^3$ and the identity 1 thus depends only on Tr u. But u is the matrix of the two-dimensional representation E_1 of Y', so Tr u is a character of this representation and depends only on the class which contains u. The set of possible geodesic distances between neighbors on {3, 3, 5} is thus implicit in the row labeled E_1 in table 1. This observation accounts for the identification of peaks in $g(\psi)$ with classes of Y′ shown in fig. 2. (The peak heights give the number of elements in each class.) Note, in particular, that nearest-neighbor distances fall in the class C_5. Inspecting eq. (2.26a) we observe that the nearest neighbors of a point form an icosahedron, so Y′ really does describe a packing of icosahedra.

We can now determine the symmetry group $G \subset SO(4)$ of polytope {3, 3, 5}, using some basic facts [15, 16] about SO(4). Consider two points $u, v \in S^3$ and multiply them on the left by $l \in S^3$

$$u \rightarrow lu , \tag{2.32a}$$

$$v \rightarrow lv , \tag{2.32b}$$

or the right by $r^{\dagger} = r^{-1}$, $r \in S^3$,

$$u \to ur^{-1}\,, \tag{2.33a}$$

$$v \to vr^{-1}\,. \tag{2.33b}$$

Because of the group structure of S^3 the results of these multiplications are new elements of S^3. It follows from eq. (2.31) that the geodesic separation is unchanged.

$$\psi(lu, lv) = \psi(ur^{-1}, vr^{-1}) = \psi(u, v)\,. \tag{2.34}$$

Thus, the transformations in eqs. (2.32) and (2.33), called left and right screws respectively, are rotations. Every rotation of S^3 is generated by a combination of left and right screws, and every pair $(l, r) \in \mathrm{SU}(2) \times \mathrm{SU}(2)$ generates a rotation [15, 16] through

$$(l, r)\colon u \to lur^{-1}\,. \tag{2.35}$$

Noting that (l, r) and $(-l, -r)$ generate the same rotation, we have the formal result

$$\mathrm{SO}(4) = [\mathrm{SU}(2) \times \mathrm{SU}(2)]/Z_2\,. \tag{2.36}$$

We can obtain a similar formula for G. For any elements l, $r \in \mathrm{Y}'$ the left and right cosets $l\mathrm{Y}'$ and $\mathrm{Y}'r^{-1}$ give the original group Y′ in a new orientation. Thus

$$\mathrm{G} = (\mathrm{Y}' \times \mathrm{Y}')/Z_2\,. \tag{2.37}$$

It follows that the order of the group G is $\mathrm{O(G)} = (120)^2/2 = 7200$. This decomposition of G will allow us to compute the projection of polytope {3, 3, 5} onto hyperspherical harmonics.

2.3. STRUCTURE FUNCTION OF POLYTOPE {3, 3, 5}

In this section we use the group G to determine the allowed values of n for which the structure function S_n of polytope {3, 3, 5} can be nonzero. We find in particular that the first $n > 0$ for which S_n need not vanish is $n = 12$. We will also discuss the matrix Q_{12,m_1m_2} for a particularly simple orientation of polytope {3, 3, 5}.

Recall the definition of Q_{n,m_1m_2} in eq. (2.12a). Expanding the integrand in irreducible representations of G (see sect. 5 for discussion of irreducible representations of G),

$$Y_{n,m_1m_2}(\hat{\boldsymbol{u}})\rho(\hat{\boldsymbol{u}}) = \sum_{\alpha\beta,ij} C_{\alpha\beta,ij}(n, m_1, m_2)\Phi_{\alpha\beta,ij}(\hat{\boldsymbol{u}})\,, \tag{2.38}$$

where ij indexes basis functions $\Phi_{\alpha\beta,ij}$ within representation $\alpha\beta$, we have

$$Q_{n,m_1m_2} = \sum_{\alpha\beta,ij} C_{\alpha\beta,ij}(n, m_1, m_2) \int \mathrm{d}\Omega_{\hat{\boldsymbol{u}}}\, \Phi_{\alpha\beta,ij}(\hat{\boldsymbol{u}})\,. \tag{2.39}$$

But the integral in eq. (2.39) is zero unless $\Phi_{\alpha\beta,ij}$ is the unit representation [28] $\Phi_A(\hat{u}) = 1$. Because S_n vanishes if all Q_{n,m_1m_2} vanish, we must determine the number of times that the expansion (2.38) contains the unit representation; S_n vanishes unless the unit representation occurs at least once.

In general the number of times that a representation R of a group H contains the irreducible representation α is [21]

$$\mathscr{A}_R^{\mathrm{H}}(\alpha)=\frac{1}{\mathrm{O(H)}}\sum_{h\in \mathrm{H}} \chi_R^{\mathrm{H}}(h)\chi_\alpha^{\mathrm{H}*}(h)\,, \tag{2.40}$$

where O(H) is the order of the group, and $\chi_R^{\mathrm{H}}(h)$ is the character of the element h of the group H in the representation R. Since $\rho(\hat{u})$ is invariant under G, we must determine the number of times that the reducible representation Y_{n,m_1m_2} contains the unit representation A of the group G. Because $\chi_A=1$ for any element of any group we have

$$\mathscr{A}_n^{\mathrm{G}}(A)=\frac{1}{\mathrm{O(G)}}\sum_{(l,r)\in G} \chi_n^{\mathrm{G}}(l,r)\,, \tag{2.41}$$

where the character χ_n^{G} of the representation Y_{n,m_1m_2} is obtained from the transformation of Y_{n,m_1m_2} under SO(4) rotations [16, 21, 27]. The basic formula is

$$Y_{n,m_1m_2}(lur^{-1})=\sum_{\substack{m_1'\\ m_2'}} D^{n/2}_{m_1m_1'}(l)\,Y_{nm_1'm_2'}(\hat{\boldsymbol{u}})D^{n/2}_{m_2'm_2}(r^{-1})\,, \tag{2.42}$$

and the corresponding character is

$$\chi_n^{\mathrm{SO(4)}}(\psi_l,\psi_r)=\sum_{m_1m_2} D^{n/2}_{m_1m_1}(l)D^{n/2}_{m_2m_2}(r^{-1}) \tag{2.43}$$

$$=\frac{\sin{(n+1)\psi_l}}{\sin{\psi_l}}\,\frac{\sin{(n+1)\psi_r}}{\sin{\psi_r}}\,, \tag{2.44}$$

where $\psi_l=\psi(l,1)$ and $\psi_r=\psi(r,1)$ are the geodesic distances of l and r from 1. Recall that the character of the lth irreducible representation of SO(3) is

$$\chi_l^{\mathrm{SO(3)}}(\theta)=\frac{\sin{(2l+1)\frac{1}{2}\theta}}{\sin{\frac{1}{2}\theta}}\,. \tag{2.45}$$

Thus

$$\chi_n^{\mathrm{SO(4)}}(\psi_l,\psi_r)=\chi_{n/2}^{\mathrm{SO(3)}}(2\psi_l)\chi_{n/2}^{\mathrm{SO(3)}}(2\psi_r)\,. \tag{2.46}$$

We can now rewrite the sum in eq. (2.41) as

$$\mathscr{A}_n^{\mathrm{G}}(A)=\left\{\tfrac{1}{120}\sum_{l\in \mathrm{Y}'} \chi_{n/2}^{\mathrm{SO(3)}}(2\psi_l)\right\}^2\,. \tag{2.47}$$

The expression in parenthesis is zero for n odd, and for n even is equal to

$$\mathscr{A}_{n/2}^{\mathrm{Y}}(A)=\tfrac{1}{60}\sum_{y\in \mathrm{Y}} \chi_{n/2}^{\mathrm{SO(3)}}(y)\,, \tag{2.48}$$

which is the number of times that the spherical harmonic $Y_{n/2,m}(\theta,\phi)$ contains the unit representation of the icosahedral group. Carrying out the sum in eq. (2.48) we find that nonzero spherical harmonics are possible for

$$n=0,\,12,\,20,\,24,\,30,\,32,\,36,\,40,\,42,\,44,\,48,\,50,\,52,\,54,\,56,\,60\,, \tag{2.49}$$

and any even $n > 60$. This result has also been obtained by Straley [29] who evaluated the integral (2.16) numerically for a delta function distribution on polytope $\{3, 3, 5\}$.

In order to compare the result (2.49) with X-ray scattering experiments we need to introduce defects, and associate wave numbers q with values of n. One possible association relies on identifying q^2 with an eigenvalue of the laplacian operator in R^3. Noting that Y_{n,m_1m_2} is an eigenfunction of the laplacian on S^3 with eigenvalue [16] $n(n+2)$ we make the association

$$q \leftrightarrow \sqrt{n(n+2)}\,. \tag{2.50}$$

The peaks in S_n at $n = 12, 20, 24$ suggest that $S(q)$ will have peaks at q_n where

$$\begin{aligned} q_2/q_1 &= \sqrt{55/21} \doteq 1.6183\,, \\ q_3/q_1 &= \sqrt{26/7} \doteq 1.9272\,. \end{aligned} \tag{2.51}$$

Experimentally [30] it is found that $q_2/q_1 \approx 1.7$ and $q_3/q_1 \approx 2.0$ for a variety of metallic glasses.

Because $n = 12$ is the lowest value of n for which S_n need not vanish, it plays a special role in the Landau theory developed in sect. 3. In particular, the order parameter is the 13×13 matrix Q_{12,m_1m_2}. It is possible that there are non-icosahedral distributions of points on S^3 for which S_n has its first peak at $n = 12$. Therefore we describe details of the matrix Q^0_{12,m_1m_2} which are unique to icosahedral distributions.

A similar calculation has been carried out for the coefficients Q_{6m} in an expansion in ordinary spherical harmonics $Y_{6m}(\theta, \phi)$ describing an icosahedron [2]. When the z-axis passes through a vertex of an icosahedron [2],

$$Q^{\mathrm{v}}_{6,m} = Q^{\mathrm{v}}_{6,0}(0, -\sqrt{\tfrac{7}{11}}, 0, 0, 0, 0, 1, 0, 0, 0, 0, \sqrt{\tfrac{7}{11}}, 0)\,. \tag{2.52}$$

Similarly when the z-axis passes through a face of an icosahedron

$$Q^{\mathrm{f}}_{6,m} = Q^{\mathrm{f}}_{6,0}(-\sqrt{\tfrac{28}{33}}, 0, 0, \sqrt{\tfrac{7}{3}}, 0, 0, 1, 0, 0, -\sqrt{\tfrac{7}{3}}, 0, 0, -\sqrt{\tfrac{28}{33}})\,. \tag{2.53}$$

We wish to see if a comparable result holds for polytope $\{3, 3, 5\}$ in some special orientation.

Thus far, we have regarded the vertices of $\{3, 3, 5\}$ as elements of Y'. An alternative tabulation of these points (corresponding to a different orientation of $\{3, 3, 5\}$) is given by a modification of Coxeter's "triacontagonal projection" [6]*

$$A_k = \mathrm{e}^{-i\sigma_z\pi k/6}\, \mathrm{e}^{\frac{1}{2}i\sigma_y\beta_a}\, \mathrm{e}^{-i\sigma_z\pi k/5}\,, \tag{2.54a}$$

$$B_k = \mathrm{e}^{-i\sigma_z\pi k/6}\, \mathrm{e}^{\frac{1}{2}i\sigma_y\beta_b}\, \mathrm{e}^{-i\sigma_z\pi k/5}\,, \tag{2.54b}$$

$$C_k = \mathrm{e}^{-i\sigma_z\pi k/6}\, \mathrm{e}^{\frac{1}{2}i\sigma_y\beta_c}\, \mathrm{e}^{-i\sigma_z\pi k/5}\,, \tag{2.54c}$$

$$D_k = \mathrm{e}^{-i\sigma_z\pi k/6}\, \mathrm{e}^{\frac{1}{2}i\sigma_y\beta_d}\, \mathrm{e}^{-i\sigma_z\pi k/5}\,, \tag{2.54d}$$

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* The triacontagonal projection used here is related to the one described by Coxeter on p. 247 of [6] by interchanging the second and fourth entries in every four-vector.

where $\beta_a = 37.377°$, $\beta_b = 79.188°$, $\beta_c = 100.822°$, and $\beta_d = 142.623°$. In eqs. (2.54a) and (2.54d), $k = 0, 2, 4, \dots, 58$. In eqs. (2.54b) and (2.54c), $k = 1, 3, 5, \dots, 59$. Using the fact that

$$D^{n/2}_{m_1 m_2}(\alpha, \beta, \gamma) = \mathrm{e}^{i\alpha m_1}\, d^{n/2}_{m_1 m_2}(\beta)\, \mathrm{e}^{i\gamma m_2}\,, \tag{2.55}$$

we can evaluate eq. (2.12a) using the points (2.54). We find that $Q_{12,m_1 m_2}$ must vanish unless

$$5m_2 - 6m_1 = 15i\,, \tag{2.56}$$

where i is an integer. The allowed pairs (m_1, m_2) have $m_1 = -5, 0, 5$ and $m_2 = -6, -3, 0, 3, 6$. In fact we have determined numerically that $Q_{12,m_1 m_2}$ factors,

$$Q^0_{12,m_1 m_2} \propto Q^{\mathrm{v}}_{6,m_1} Q^{\mathrm{f}}_{6,m_2} \tag{2.57}$$

although we have not succeeded in deriving this simple result. Thus if a particle distribution is icosahedral then the matrix $Q_{12,m_1 m_2}$ must be the matrix $Q^0_{12,m_1 m_2}$ (eq. (2.57)) transformed by some rotation. In particular, we find that $Q_{12,m_1 m_2} \propto Q^{\mathrm{v}}_{6,m_1} Q^{\mathrm{v}}_{6,m_2}$ when the vertices of {3, 3, 5} are in the orientation Y′.

The calculations of this section are readily extended to determine the allowed n's for polytopes based on {3, 3, 5} with more than one atom per unit cell. "Polytope 240" [10, 11], for example, has an atom at some position τ on S^3 within the unit cell surrounding an atom at 1, and at 119 similar positions in the other unit cells. It is straightforward to show in this case that

$$Q_{n,m_1 m_2} \to \sum_m \left[\delta_{m_1 m} + D^{n/2}_{m_1 m}(\tau)\right] Q_{n,m m_2}\,. \tag{2.58}$$

3. Landau theory

In sect. 2, we showed how to characterize the extended icosahedral order present in polytope {3, 3, 5}. There is a natural generalization of this point of view which allows one to define a local order parameter for glasses and supercooled liquids in flat space. Using this description, one can construct a uniformly frustrated Ginzburg–Landau model of the statistical mechanics. Because the magnitude of the order parameter can vary, this approach can be used at both high and low temperatures. Since the order parameter vanishes on disclination lines, magnitude fluctuations will also be important when one coarse grains over regions containing many defects. When amplitude fluctuations are neglected, our description is similar to a continuum elastic theory proposed by Sethna [14]. In this limit, only the phase degrees of freedom in the order parameter matter. Both theories have a nonzero density of defect lines in the ground state, and are very likely to have glassy metastable states.

Before proceeding further, it is useful to recapitulate Landau's description of incipient crystalline order in a liquid [23]. Suppose we know that a lattice with reciprocal lattice vectors $\{\boldsymbol{G}\}$ is about to emerge from a disordered liquid with decreasing temperature. Although there is no long-range order, we can define a set of local order parameters $\rho_G(\boldsymbol{r})$ by restricting the domain of integration in eq. (2.2) to a volume ΔV centered at the point $\boldsymbol{r}$,

$$\rho_{G}(\boldsymbol{r})=\frac{1}{\Delta V}\int \mathrm{d}^3\boldsymbol{r}'\,\mathrm{e}^{i\boldsymbol{G}\cdot\boldsymbol{r}'}\rho(\boldsymbol{r}')\,. \tag{3.1}$$

The volume ΔV must be larger than a lattice constant, but small compared to the macroscopic system size. For simplicity we approximate density variations in the material using a restricted summation Σ' over the subset of smallest nonzero reciprocal lattice vectors,

$$\rho(\boldsymbol{r})=\rho_0+\mathrm{Re}\left\{\sum_{\boldsymbol{G}}{}'\,\rho_{\boldsymbol{G}}(\boldsymbol{r})\,\mathrm{e}^{-i\boldsymbol{G}\cdot\boldsymbol{r}}\right\}, \tag{3.2}$$

where ρ_0 is the density in a uniform liquid. Henceforth, all summations over $\boldsymbol{G}$ will be restricted to this subset.

To construct a translationally and rotationally invariant free energy from the $\rho_{\boldsymbol{G}}(\boldsymbol{r})$'s, we first note that, under a uniform translation of space $\boldsymbol{r}\to\boldsymbol{r}-\boldsymbol{u}_0$, it follows from (3.2) that

$$\rho_{\boldsymbol{G}}(\boldsymbol{r})\to\mathrm{e}^{i\boldsymbol{G}\cdot\boldsymbol{u}_0}\rho_{\boldsymbol{G}}(\boldsymbol{r})\,. \tag{3.3a}$$

Under a uniform rotation about the origin, $\boldsymbol{r}\to R_{\hat{\boldsymbol{n}}}(\theta)\boldsymbol{r}$, we have

$$\rho_{\boldsymbol{G}}(\boldsymbol{r})\to\exp\{i\boldsymbol{G}\cdot[R_{\hat{\boldsymbol{n}}}(\theta_0)-1]\boldsymbol{r}\}\rho_{\boldsymbol{G}}(\boldsymbol{r})\,. \tag{3.3b}$$

The 3×3 matrix R is $R=\exp[i\theta_0(\boldsymbol{l}\cdot\boldsymbol{n})]$, where the l_i are generators of SO(3) rotations. In the limit of infinitesimal $\boldsymbol{u}_0$ and $\boldsymbol{\theta}_0=\theta_0\hat{\boldsymbol{n}}$, which avoids complications associated with the noncommutivity of translations and rotations, the net effect on the order parameter $\rho_{\boldsymbol{G}}(\boldsymbol{r})$ is

$$\rho_{\boldsymbol{G}}(\boldsymbol{r})\to\mathrm{e}^{i\boldsymbol{G}\cdot\boldsymbol{u}_0+i\boldsymbol{G}\cdot(\boldsymbol{\theta}_0\times\boldsymbol{r})}\rho_{\boldsymbol{G}}(\boldsymbol{r})\,. \tag{3.3c}$$

Eq. (3.3c) suggests that the important degrees of freedom will be an order parameter amplitude and six slowly varying "phases" $\boldsymbol{u}(r)$ and $\boldsymbol{\theta}(r)$, corresponding to the six generators of translations and rotations in a solid. A free energy density, including gradient terms, which is translationally invariant, and rotationally invariant to lowest order in $\boldsymbol{\theta}$ is [25]

$$\begin{aligned}\mathscr{F}={}&\tfrac{1}{2}K_0\sum_{\boldsymbol{G}}|(\boldsymbol{\nabla}-i\boldsymbol{G}\times\boldsymbol{\theta})\rho_{\boldsymbol{G}}|^2+\tfrac{1}{2}r\sum_{\boldsymbol{G}}|\rho_{\boldsymbol{G}}|^2\\ &+w\sum_{\boldsymbol{G}_1+\boldsymbol{G}_2+\boldsymbol{G}_3=0}\rho_{\boldsymbol{G}_1}\rho_{\boldsymbol{G}_2}\rho_{\boldsymbol{G}_3}+\mathrm{O}(\rho_{\boldsymbol{G}}^4)\,.\end{aligned} \tag{3.4}$$

The peculiar gradient coupling is required by rotational invariance. If fluctuations can be neglected, the cubic term leads to a first-order freezing transition for sufficiently negative quadratic couplings r. At low temperatures $\boldsymbol{\theta}$ becomes locked to the curl of the phonon displacement field [25]

$$\boldsymbol{\theta}(\boldsymbol{r})=\tfrac{1}{2}\boldsymbol{\nabla}\times\boldsymbol{u}(\boldsymbol{r})\,, \tag{3.5}$$

so that the orientational degrees of freedom drop out of the problem. This locking is quite analogous to the Higgs mechanism. At low temperatures, we expect that $\rho_G(\boldsymbol{r})$ depends only on a slowly varying displacement field $\boldsymbol{u}(\boldsymbol{r})$,

$$\rho_G(\boldsymbol{r}) = |\rho_G^{\circ}|\, \mathrm{e}^{i\boldsymbol{G}\cdot\boldsymbol{u}(\boldsymbol{r})}\,, \tag{3.6}$$

where the amplitude $|\rho_G^{\circ}|$ is independent of the direction of $\boldsymbol{G}$. Assuming for simplicity an isotropic distribution of $\boldsymbol{G}$'s, it is straightforward to show that $\mathscr{F}$ then becomes

$$\mathscr{F} = \mathrm{const} + \tfrac{1}{2}K \int \mathrm{d}^3 r [\partial_i u_j - \varepsilon_{ijk}\theta_k]^2\,, \tag{3.7}$$

with $K \propto |\rho_G^{\circ}|^2 K_0$, which exhibits the locking of θ_k to gradients of u_j explicitly. Using eq. (3.5) to eliminate θ_k, we recover the standard continuum elastic description of a crystal, expressed in terms of the symmetrized strain tensor $u_{ij} = \frac{1}{2}(\partial_i u_j + \partial_j u_i)$ [26].

As discussed in sect. 2.3, order in a {3, 3, 5} crystal can be characterized by the Fourier coefficients Q_{12,m_1,m_2}. As illustrated in fig. 3, we can define a *local* order parameter $Q_{12,m_1m_2}(\boldsymbol{r})$ in flat space via stereographic projection onto a featureless, tangent four-dimensional sphere. The radius of the sphere is chosen so that it can just accommodate 120-particles in the configuration of {3, 3, 5} with geodesic separation equal to the flat space near neighbor separation. The order parameter associated with a small volume ΔV of particles centered at r is given by a modification of eq. (2.12a),

$$Q_{12,m_1m_2}(\boldsymbol{r}) = \int_{\Delta V'} \mathrm{d}\Omega_{\hat{\boldsymbol{u}}}\, Y_{12,m_1m_2}(\hat{\boldsymbol{u}})\rho(\hat{\boldsymbol{u}})\,, \tag{3.8}$$

where $\rho(\hat{\boldsymbol{u}})$ is the projected particle density, and the domain of angular integration is restricted to the projection $\Delta V'$ of ΔV. Sethna [14] has used a similar sphere with the polytope {3, 3, 5} inscribed on it to formulate a continuum elastic theory.

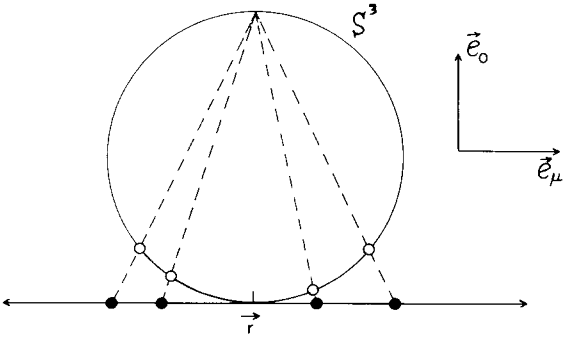

Fig. 3. Projection of particle configuration at $\boldsymbol{r}$ onto S^3.

Under an SO(4) rotation of the coordinate axes $(\boldsymbol{e}_0, \boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z)$, the change in $Q_{12,m_1 m_2}$ is given by an SO(4) representation matrix [16]

$$Q_{12,m} \xrightarrow{R \in \mathrm{SO}(4)} \sum_{m'} \Delta^{(12)}_{mm'} Q_{12,m'} \,. \tag{3.9}$$

Here, we have used the notations $m \equiv (m_1, m_2)$ and $m' \equiv (m'_1, m'_2)$ to denote pairs of variables each of which runs from -6 to $+6$. The indices m and m' can assume 169 different values. The matrix $\Delta^{(12)}_{m,m'}$ can be expressed in terms of SU(2) Wigner matrices using the homeomorphism between SO(4) and SU(2)×SU(2). If a rotation $R \in \mathrm{SO}(4)$ is characterized by the pair of elements $(l, r) \equiv (-l, -r)$, we find from eq. (2.42)

$$\Delta^{(12)}_{m_1 m_2, m'_1 m'_2}(l, r) = D^{(6)}_{m_1 m'_1}(l) D^{(6)}_{m'_2 m_2}(r^{-1}) \,. \tag{3.10}$$

Alternatively, we can write,

$$\underset{\approx}{\Delta}^{(12)} = \exp\left[i \sum_{\alpha=1}^{6} \theta_\alpha \underset{\approx}{L}^{(12)}_\alpha \right] , \tag{3.11}$$

where the $L^{(12)}_\alpha$ are the six generators of the $n = 12$ representation [27] of SO(4). These generators can be labelled by the six possible rotation planes $(0, x)$, $(0, y)$ $(0, z)$, (y, z), (x, z) and (x, y). The generators $\underset{\approx}{L}^{(12)}_{\mu\nu}$, where μ and ν are distinct cartesian components x, y or z, correspond to the generators of rotations in flat space, while the generators $\underset{\approx}{L}^{(12)}_{0\mu}$ are analogous to generators of flat space translations.

An SO(4)-invariant Landau free-energy density constructed from the order parameter $Q_{12,m_1 m_2}(\boldsymbol{r})$ is

$$\begin{aligned} \mathscr{F} = {} & \tfrac{1}{2} K \sum_m |(D_\mu Q_{12,m})|^2 + \tfrac{1}{2} r \sum_m |Q_{12,m}|^2 \\ & + w \sum_{\substack{m_1, m_2, m_3 \\ m'_1, m'_2, m'_3}} \begin{pmatrix} 6 & 6 & 6 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} 6 & 6 & 6 \\ m'_1 & m'_2 & m'_3 \end{pmatrix} Q_{12,m_1 m'_1} Q_{12,m_2 m'_2} Q_{12,m_3 m'_3} + \mathcal{O}(Q^4_{12}) \,. \end{aligned} \tag{3.12}$$

The third order term is constructed from the standard SO(3) Wigner $3j$-symbols [28]; its SO(4) rotational invariance follows from (3.9) and (3.10) and the properties of the 3-j symbols. The gradient term in eq. (3.12) is a kind of matrix "covariant derivative",

$$(D_\mu Q_{12})_m = \sum_{m'} [\delta_{m,m'} \partial_\mu - i\kappa (L^{(12)}_{0\mu})_{m,m'}] Q_{12,m'} \,. \tag{3.13}$$

Following ref. [14], we have constructed this derivative so that the ground state is obtained when adjacent particle configurations are related by "rolling" a reference polytope {3, 3, 5} with radius κ^{-1} along a straight line joining them. Indeed, solving the equation $(D_\mu Q_{12})_m = 0$ along a small separation vector $\boldsymbol{\delta}$ gives a preferred relationship between $Q_{12,m}(\boldsymbol{r} + \boldsymbol{\delta})$ and $Q_{12,m}(\boldsymbol{r})$, namely

$$\boldsymbol{Q}_{12}(\boldsymbol{r} + \boldsymbol{\delta}) = \mathrm{e}^{i\kappa \underset{\approx}{L}^{(12)}_{0\mu} \delta^\mu} \boldsymbol{Q}_{12}(\boldsymbol{r}) \,. \tag{3.14}$$

For notational convenience, we have written $Q_{12,m}$ as a 169-component vector. Note that the sign of the $i\kappa$ term in eq. (3.13) is at our disposal, since it can be changed by reflecting the tangent sphere through the hyperplane spanned by $\boldsymbol{e}_x$, $\boldsymbol{e}_y$, and $\boldsymbol{e}_z$.

At low temperatures, in analogy with a closely related analysis of orientational spherical harmonics by Steinhardt et al. [2], we expect that the polynomial part of eq. (3.12) is minimized when $Q_{12,m} = Q^0_{12,m}$ where $Q^0_{12,m}$ is the special set of $n = 12$ Fourier coefficients determined (up to an SO(4) rotation) by the configuration {3, 3, 5} (see sect. 2.3). In this limit, it makes sense to substitute

$$\boldsymbol{Q}_{12}(\boldsymbol{r}) = \exp\left[i \sum_{\alpha=1}^{6} \theta_\alpha(\boldsymbol{r}) \underset{\approx}{L}{}_\alpha^{(12)} \right] \boldsymbol{Q}^0_{12} \tag{3.15}$$

into (3.12), and obtain a theory parametrized by the six SO(4) Euler angles $\theta_\alpha(\boldsymbol{r})$. The energetics then depend only on the gradient term, and the resulting theory is almost identical to the continuum elastic approach of Sethna. In contrast to the 4×4 SO(4) matrices used in ref. [14], however, the 169×169 representation matrices used here respect the symmetries of the polytope {3, 3, 5}. This difference is important, for example, to properly account for defects in lattice discretizations of the theory.

It is interesting to compare eq. (3.12) with the Landau expansion (3.4) for a flat space crystalline solid. Both theories have cubic terms suggesting first-order phase transitions in equilibrium. The Euler angles $\theta_\alpha(\boldsymbol{r})$ are reminiscent of the translational and orientational phases $\boldsymbol{u}(\boldsymbol{r})$ and $\boldsymbol{\theta}(\boldsymbol{r})$ entering (3.4). A crucial difference, however, is that eq. (3.12) is frustrated – it is impossible to make the gradient term vanish everywhere without introducing defects.

To characterize this frustration more precisely, let us follow the order parameter around the small square plaquette (μ, ν) with area a^2 shown in fig. 4. Assuming that $\boldsymbol{Q}_{12}(\boldsymbol{r})$ is given, we can make the gradient term vanish along this contour by requiring that $\boldsymbol{Q}_{12}$ at successive points on the plaquette be given by eq. (3.14). The net change in $\boldsymbol{Q}_{12}(\boldsymbol{r})$ is given by

$$\boldsymbol{Q}_{12}(\boldsymbol{r}) \to \underset{\approx}{\Delta}{}^{(12)}_{0\mu}(\kappa a)\underset{\approx}{\Delta}{}^{(12)}_{0\nu}(\kappa a)\underset{\approx}{\Delta}{}^{(12)}_{0\mu}(-\kappa a)\underset{\approx}{\Delta}{}^{(12)}_{0\nu}(-\kappa a)\boldsymbol{Q}_{12}(\boldsymbol{r}), \tag{3.16a}$$

where the representation matrices are

$$\underset{\approx}{\Delta}{}_{0\mu}(\kappa a) \equiv \exp\left[i\kappa a \underset{\approx}{L}{}^{(12)}_{0\mu} \right]. \tag{3.16b}$$

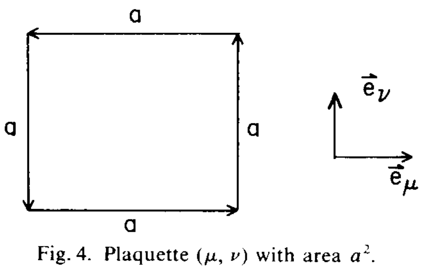

Fig. 4. Plaquette (μ, ν) with area a^2.

Frustration is present because the order parameter will not in general return to its initial value. Indeed, it is easy to show that

$$\underset{\approx}{\Delta}{}^{(12)}_{0\mu}(\kappa a)\underset{\approx}{\Delta}{}^{(12)}_{0\nu}(\kappa a)\underset{\approx}{\Delta}{}^{(12)}_{0\mu}(-\kappa a)\underset{\approx}{\Delta}{}_{0\nu}(-\kappa a) \approx 1-\kappa^2 a^2[\underset{\approx}{L}{}^{(12)}_{0\mu}, \underset{\approx}{L}{}^{(12)}_{0\nu}]$$
$$= \underset{\approx}{\Delta}{}^{(12)}_{\mu\nu}(-\kappa^2 a^2) + \mathrm{O}(\kappa^3 a^3)\,, \qquad (3.17\mathrm{a})$$

where

$$\underset{\approx}{\Delta}{}^{(12)}_{\mu\nu}(-\kappa^2 a^2) \equiv \exp[-i\kappa^2 a^2 \underset{\approx}{L}{}^{(12)}_{\mu\nu}]\,. \qquad (3.17\mathrm{b})$$

We have used units such that the SO(4) angular momentum operators are dimensionless and obey the commutation relations [27]

$$[L_{0\mu}, L_{0\nu}] = iL_{\mu\nu}\,. \qquad (3.18)$$

The remaining commutators may be written [27]

$$[L_\mu, L_\nu] = i\varepsilon_{\mu\nu\lambda}L_\lambda\,, \quad [L_\mu, L_{0\nu}] = i\varepsilon_{\mu\nu\lambda}L_{0\lambda}\,, \qquad (3.19)$$

where L_μ is a conventional SO(3) angular momentum operator,

$$L_\mu \equiv \tfrac{1}{2}\varepsilon_{\mu\nu\lambda}L_{\nu\lambda}\,. \qquad (3.20)$$

Eq. (3.17) makes it clear that the order parameter must have rotated in the plane (μ, ν) by an amount proportional to the area of the plaquette after it traverses the contour in fig. 4. Such a rotation can be accommodated by threading through a finite density κ^2 of −72° wedge disclination lines oriented normal to the plaquette [12].

The noncommutivity of the angular momentum generators plays a crucial role in generating the frustration. If the operators $L^{(12)}_{0\mu}$ behaved like c-numbers, the term analogous to a vector potential in eq. (3.13) could be eliminated by the change of variables

$$\boldsymbol{Q}_{12}(\boldsymbol{r}) = \mathrm{e}^{i\kappa \underset{\approx}{L}{}^{(12)}_{0\mu} r_\mu}\boldsymbol{Q}'_{12}(\boldsymbol{r})\,. \qquad (3.21)$$

Physically, this change of variables means the order is now measured relative to a reference {3, 3, 5} template which has been rolled in straight lines out from the origin in all directions. At low temperatures, we might then expect that $\boldsymbol{Q}'$ could be parametrized by an amplitude $\boldsymbol{Q}_0$ and a slowly varying set of small displacements $\boldsymbol{u}(r)$

$$\boldsymbol{Q}'_{12}(\boldsymbol{r}) = \mathrm{e}^{i\kappa \underset{\approx}{L}{}^{(12)}_{0\mu} u_\mu(\boldsymbol{r})}\boldsymbol{Q}_0\,, \qquad (3.22)$$

in analogy with eq. (3.6). This correspondence makes it clear that the matrices

$$\{\underset{\approx}{G}{}_{0\mu}\} = \{\kappa\underset{\approx}{L}{}^{(12)}_{0\mu}, \kappa\underset{\approx}{L}{}^{(20)}_{0\mu}, \kappa\underset{\approx}{L}{}^{(24)}_{0\mu}, \ldots\}\,. \qquad (3.23)$$

play the role of reciprocal lattice vectors in this approach. It is their noncommutivity (with commutators scaling like the inverse radius κ of the polytope) which makes the physics of glasses nontrivial.

The partition function associated with the Landau theory (3.12) is given by a functional integral over the field $\boldsymbol{Q}(\boldsymbol{r})$

$$Z = \int \mathcal{D}\boldsymbol{Q}(\boldsymbol{r}) \exp\left[-\frac{1}{k_B T}\int \mathrm{d}^3 r \mathcal{F}(\boldsymbol{r})\right]. \tag{3.24}$$

At low temperatures, we expect the statistical mechanics to be dominated by a regular lattice of −72° disclination lines, as in the Frank–Kasper phases of transition metal alloys [12]. The high temperature liquid should have defect lines of both signs, with a bias to accommodate the frustration. In equilibrium, there is probably a first-order transition connecting these phases. If the liquid is cooled rapidly, however, one might expect complicated "glassy" metastable states, consisting of tangled arrays of defect lines. Entanglement upon cooling is suggested by strong topological constraints on the crossing of −72° disclination lines at low temperatures [12].

We expect that similar Ginzburg–Landau theories can be constructed for covalently bonded amorphous systems. More generally, we can use an order parameter $Q_{p,m_1m_2}(\boldsymbol{r})$, where p is the first nonvanishing entry (other than $n=0$) in the expansion (2.7).

4. Defects

Disclination line defects in a predominantly icosahedral medium were studied in ref. [12]. The algebra of such defects is given by the homotopy group

$$\pi_1(\mathrm{SO}(3)/\mathrm{Y}) = \mathrm{Y}', \tag{4.1}$$

where Y′ is the 120-element subgroup of SU(2) whose properties were summarized in sect. 2.2. At low temperatures, the curvature mismatch between flat space and the polytope {3, 3, 5} forces in an uncompensated density of −72° wedge disclination lines. Both plus and minus 72° disclination lines appear in a microscopic Voronoi construction which counts the number of tetrahedra surrounding every near-neighbor bond [12].

Disclinations are defects in an orientational subgroup of the symmetries of the order parameter discussed in sects. 2 and 3. It is of some interest to classify the defects associated with the full symmetry group of this order parameter. An analogous problem arises in flat space crystalline solids, where translational dislocation defects are possible, as well as disclinations in the orientational order. The symmetry group of the order parameter $Q_{12,m_1m_2}(\boldsymbol{r})$ is SO(4) modulo the symmetry group of G of {3, 3, 5}. According to ref. [20], the algebra of line defects (there are no stable point defects) is given by

$$\pi_1(\mathrm{SO}(4)/\mathrm{G}) = \mathrm{G}', \tag{4.2}$$

where G′ is the (two-to-one) lift of G into the cover group of SO(4). Since the cover group of SO(4) is SU(2)×SU(2), and we know from sect. 2.2 that $G=(Y'\times Y')/Z_2$, we clearly have

$$G'=Y'\times Y'\,. \tag{4.3}$$

According to eq. (4.3), line defects in a glass can be labelled by a pair (l, r) of SU(2) matrix charges, where l and r are in Y′. In contrast to the group G, (l, r) and $(-l, -r)$ are now distinct elements. The laws of combination are given by the class multiplication table for G′ [20]. This in turn follows from the class multiplication table for Y′ worked out in ref. [12]. Disclinations are given by diagonal elements of the form (l, l) in the direct product. This identification follows by noticing [15] that if

$$l=\mathrm{e}^{\frac{1}{2}i(\hat{\boldsymbol{n}}\cdot\boldsymbol{\sigma})\theta}\,, \tag{4.4}$$

the 4×4 SO(4) matrix which produces the lifted elements (l, l) and $(-l, -l)$ is

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & & & \\ 0 & & R_{\hat{n}}(\theta) & \\ 0 & & & \end{pmatrix}, \tag{4.5}$$

where $R_{\hat{n}}(\theta)$ is a 3×3 SO(3) rotation matrix. The SO(4) matrix in eq. (4.5) describes the motion of the reference polytope {3, 3, 5} as one traverses a closed counterclockwise circuit surrounding the defect line [20]. Evidently, the polytope rotates in one of the "physical" planes (μ, ν), with the axes $\boldsymbol{e}_0$ and $\boldsymbol{e}_{\hat{n}}$ held fixed. The rotation angle varies continuously from 0 to θ for the defect (l, l), and from 0 to $\theta\pm 2\pi$ for the defect $(-l, -l)$. The subgroup of diagonal elements (l, l) of G′ is, of course, just the group Y′ studied in ref. [12].

It is also of interest to consider defects of the form (l, l^{-1}). One can show that the corresponding SO(4) matrix represents a rotation of the polytope in the plane spanned by $\boldsymbol{e}_0$ and $\boldsymbol{e}_{\hat{n}}$ as one moves around the defect. Since these rotations can be described by the "translational" generators $L_{0\mu}$ of SO(4), it seems appropriate to call such defects "dislocations". Two additional types of defect may be written $(1, r)$ and $(l, 1)$. The associated SO(4) matrices represent right and left screw symmetry operations [15], which have no simple analog in SO(3). This symmetry is closely related to the twisted "Bernal spiral" of perfect tetrahedra shown in fig. 20 of ref. [12]. Since

$$(l, r)=(p, 1)(r, r)\,, \tag{4.6}$$

where $pr=l$, any defect can be decomposed into a disclination and a left (or right) screw.

At low temperatures, the frustration embodied in the free energy (3.12) forces in defects of the type $(\mathrm{e}^{\frac{1}{2}i\theta_0\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}}, \mathrm{e}^{\frac{1}{2}i\theta_0\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}})$ where $\theta_0=-2\pi/5$, and $\hat{\boldsymbol{n}}$ if directed along the axis of the disclination line. When two such defect lines (α, α) and (β, β) try to cross, they will in general create an umbilical line (γ, γ) joining them, given by [20]

$$\begin{aligned}(\gamma, \gamma) &= (\alpha, \alpha)(\beta, \beta)(\alpha, \alpha)^{-1}(\beta, \beta)^{-1} \\ &= (\alpha\beta\alpha^{-1}\beta^{-1}, \alpha\beta\alpha^{-1}\beta^{-1}) . \end{aligned} \tag{4.7}$$

As discussed in ref. [12] in the context of the group Y′, two lines corresponding to −72° rotations about different axes will always produce another −72° line joining them. This observation is the basis of the "entanglement" phenomenon referred to at the end of sect. 3.

5. Tight binding model

In sect. 2 we have analyzed structural properties of the perfect icosahedral crystal polytope {3, 3, 5}. In this section we diagonalize a tight binding hamiltonian in order to elucidate the corresponding electronic properties. Calculations have been carried out numerically [11] on a "decorated" version of polytope {3, 3, 5} which is expected to model amorphous silicon*. We choose to solve the simpler model

$$\mathcal{H} = -t \sum_{u\in \mathrm{Y}'} \sum_{\mathrm{n.n.}(u)} |u\rangle\langle \mathrm{n.n.}\,(u)| , \tag{5.1}$$

where t is a hopping matrix element and n.n. $(u) \in \mathrm{Y}'$ denotes a nearest-neighbor of $u \in \mathrm{Y}'$. We carry out our calculation exactly using the full symmetry group G.

In fig. 2 we see that the nearest neighbors of 1 comprise the class C_5. Thus the nearest-neighbors of $u \in \mathrm{Y}'$ are vu where $v \in C_5$, and

$$\mathcal{H} = -t \sum_{u\in \mathrm{Y}'} \sum_{v \in C_5} |u\rangle\langle vu| . \tag{5.2}$$

Because the hamiltonian (5.2) is invariant under any transformation in G, and because G is transitive on the basis functions $\{|u\rangle\colon u \in \mathrm{Y}'\}$, a generalization of Bloch's theorem tells us that eigenfunctions of $\mathcal{H}$ are basis functions of irreducible representations of G. We shall now determine the representations generated by eigenfunctions of (5.2).

The relationship (2.37) between G and Y′ allows us to express irreducible representations and characters of G in terms of irreducible representations and characters of Y′. Warner [31] displays the full character table of G. We shall exploit the following facts. Irreducible representations of G with dimension $d_{\alpha\beta}$ are generated by

$$\phi_{\alpha\beta,ij} = \phi_{\alpha,i}\phi_{\beta,j} , \tag{5.3}$$

where $\phi_{\alpha i}$ and $\phi_{\beta j}$ generate irreducible representations of Y′ with dimensions d_α and d_β, and $d_{\alpha\beta} = d_\alpha d_\beta$. We call the representation generated by $\Phi_{\alpha\beta,ij}$ "diagonal" when $\alpha = \beta$ and "off diagonal" when $\alpha \neq \beta$.

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* In these references the symmetries of abelian subgroups of G are used to partially diagonalize tight binding hamiltonians.

Only the diagonal representations of G are relevant to the hamiltonian (5.2). To see this, consider the 120-dimensional representation R generated by the tight binding basis functions $|u\rangle$ centered at each vertex $u \in \mathrm{Y}'$. The character of (l, r) in this representation is the number of vertices that are stationary under $u \to lur^{-1}$. Note that if u is stationary then $l = uru^{-1}$ so l and r must belong to the same class. Thus we have

$$\chi_R^{\mathrm{G}}(l, r) = \delta_{A,B}\mathrm{O}(\mathrm{Y}')/\mathrm{O}(A)\,, \tag{5.4}$$

where A and B are the classes of Y′ containing l and r, and O(Y′) and O(A) are the number of elements in Y′ and A. Any eigenfunction of $\mathcal{H}$ is a sum of tight binding basis functions centered on the vertices $\in \mathrm{Y}'$ and is thus expressible in terms of the basis of the representation R. We can apply eq. (2.40) to determine which irreducible representations of G are contained in R,

$$\mathcal{A}_R^{\mathrm{G}}(\alpha\beta) = \frac{1}{\mathrm{O(G)}} \sum_{(l,r)\in \mathrm{G}} \chi_R^{\mathrm{G}}(l, r)\chi_{\alpha\beta}^{\mathrm{G}*}(l, r)\,. \tag{5.5}$$

The only terms in the sum which are nonzero have l, r both elements of the same class of Y′. But when this is true we have

$$\chi_{\alpha\beta}^{\mathrm{G}}(l, r) = \chi_\alpha^{\mathrm{Y}'}(l)\chi_\beta^{\mathrm{Y}'}(r)\,, \tag{5.6}$$

which, when combined with eq. (5.4) yields

$$\mathcal{A}_R^{\mathrm{G}}(\alpha\beta) = \frac{1}{\mathrm{O}(\mathrm{Y}')} \sum_{l\in \mathrm{Y}'} \chi_\alpha^{\mathrm{Y}'}(l)\chi_\beta^{\mathrm{Y}'}(l)\,. \tag{5.7}$$

This equation is just the dot product of two rows in the character table of Y′ and hence [28]

$$\mathcal{A}_R^{\mathrm{G}}(\alpha\beta) = \delta_{\alpha,\beta}\,. \tag{5.8}$$

Thus we see that the representation R contains each diagonal irreducible representation of G precisely once. This is the result expressed in eq. (1.4) which is a sum over α of $d_{\alpha\alpha} = d_\alpha^2$ and should be recognized also in the sum rule (2.29).

Construction of wave functions and evaluation of energies involves some algebraic manipulations which we outline here. A characteristic wave function of representation $\Phi_{\alpha\alpha,ij}$ is [28]

$$\psi_{\alpha\alpha} = \frac{1}{\mathrm{O(G)}} \sum_{(l,r)\in \mathrm{G}} \chi_{\alpha\alpha}^{\mathrm{G}}(l, r)|lr^{-1}\rangle\,. \tag{5.9}$$

It is useful to rewrite this in terms of components $v \in \mathrm{Y}'$

$$\psi_{\alpha\alpha} = \sum_{v\in \mathrm{Y}'} C_{\alpha\alpha}(v)|v\rangle\,, \tag{5.10}$$

where

$$C_{\alpha\alpha}(v) = \frac{1}{2\,\mathrm{O(G)}} \sum_{u\in \mathrm{Y}'} \chi_{\alpha\alpha}^{\mathrm{G}}(u, v^{-1}u) \tag{5.11}$$

noting that $2\,\mathrm{O(G)} = (120)^2$, $C_{\alpha\alpha}(1) = 1/120$ for all α.

Because $\psi_{\alpha\alpha}$ is an eigenfunction of $\mathcal{H}$ we have

$$E_\alpha \psi_{\alpha\alpha} = \mathcal{H}\psi_{\alpha\alpha} . \tag{5.12}$$

Using the form (5.2) to represent $\mathcal{H}$, and projecting both sides of (5.12) onto $\langle 1|$ we find

$$E_\alpha C_{\alpha\alpha}(1) = -t \sum_{v \in C_5} C_{\alpha\alpha}(v) . \tag{5.13}$$

Using the fact that

$$\chi^{\mathrm{G}}_{\alpha\alpha}(l, r) = \chi^{\mathrm{Y}'}_{\alpha}(l)\chi^{\mathrm{Y}'}_{\alpha}(r^{-1}) \tag{5.14}$$

to rewrite eq. (5.11) we conclude

$$E_\alpha = \frac{-t}{120} \sum_{\substack{u \in \mathrm{Y}' \\ v \in C_5}} \chi^{\mathrm{Y}'}_{\alpha}(u)\chi^{\mathrm{Y}'}_{\alpha}(u^{-1}v) . \tag{5.15}$$

Because the character $\chi^{\mathrm{Y}'}_{\alpha}(u)$ depends only on the conjugacy class A which contains u we can rewrite (5.15) as

$$E_\alpha = \frac{-t}{120} \sum_{A} \chi^{\mathrm{Y}'}_{\alpha}(A) \sum_{u \in A} \sum_{v \in C_5} \chi^{\mathrm{Y}'}_{\alpha}(u^{-1}v) . \tag{5.16}$$

Further simplification is achieved by noting that

$$\sum_{u \in A} \sum_{v \in C_5} \chi^{\mathrm{Y}'}_{\alpha}(u^{-1}v) = \mathrm{Tr}\left\{ \sum_{u \in A} \sum_{v \in C_5} \underset{\approx}{T}^{\alpha}(u^{-1})\underset{\approx}{T}^{\alpha}(v) \right\} , \tag{5.17}$$

where $\underset{\approx}{T}^{\alpha}(v)$ is the matrix of the representation $\phi_{\alpha i}$ for the group element $v \in \mathrm{Y}'$. Making use of the identity [21]

$$\sum_{u \in A} \underset{\approx}{T}^{\alpha}(u^{-1}) = \underset{\approx}{1}_{\alpha} \mathrm{O}(A)\chi^{\mathrm{Y}'}_{\alpha}(A)/d_\alpha , \tag{5.18}$$

when $\underset{\approx}{1}_{\alpha}$ is the identity matrix of dimension d_α, we find

$$\sum_{u \in A} \sum_{v \in C_5} \chi^{\mathrm{Y}'}_{\alpha}(u^{-1}v) = \mathrm{O}(A)\mathrm{O}(C_5)\chi^{\mathrm{Y}'}_{\alpha}(A)\chi^{\mathrm{Y}'}_{\alpha}(C_5)/d_\alpha . \tag{5.19}$$

We can use this result to write

$$E_\alpha = \left\{ -\frac{12t\chi^{\mathrm{Y}'}_{\alpha}(C_5)}{d_\alpha} \right\}\left\{ \frac{1}{\mathrm{O}(\mathrm{Y}')} \sum_{A} \mathrm{O}(A)[\chi^{\mathrm{Y}'}_{\alpha}(A)]^2 \right\} . \tag{5.20}$$

The second factor in eq. (5.20) is the dot product of a single row in the character table of Y′ with itself, and thus equals 1. Finally, we have

$$E_\alpha = -12t\chi^{\mathrm{Y}'}_{\alpha}(C_5)/d_\alpha . \tag{5.21}$$

The same methods are easily extended to a general, rotationally invariant, tight binding hamiltonian of the form

$$\mathcal{H} = -\sum_{A} t_A \sum_{u \in \mathrm{Y}'} \sum_{v \in A} |u\rangle\langle vu| , \tag{5.22}$$

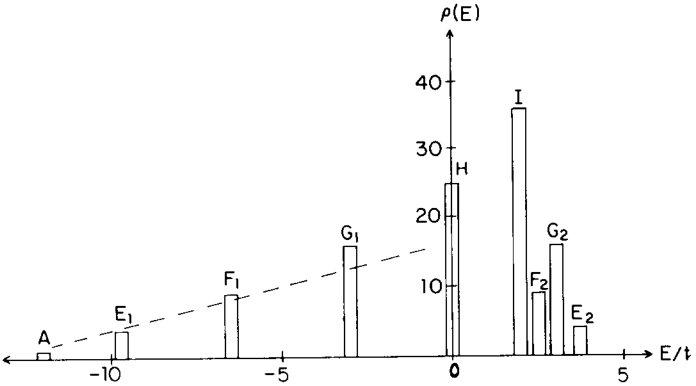

Fig. 5. Density of states $\rho(E)$ from eq. (5.21). Dashed line shows the prediction of the free electron model.

where the first sum is over the nine classes A of Y′. The eigenenergies are

$$E_\alpha = -\sum_A t_A \mathrm{O}(A) \chi^{\mathrm{Y}'}_\alpha(A)/d_\alpha \,. \tag{5.23}$$

Fig. 5 shows a histogram density of states computed from eq. (5.21). Peaks are labelled according to the irreducible representation formal by sets of degenerate wave functions. The peak height is just $d_{\alpha\alpha} = d^2_\alpha$, the degeneracy of the irreducible representation. These results agree with numerical calculations by Warner [32].

Note the linear growth in the density of states near the low-energy band edge. This can be understood in the context of a free electron model on S^3 for which, in dimensionless units, $E_n = n(n+2)$ and $d_{nn} = (n+1)^2$. (The eigenfunctions are just the hyperspherical harmonics Y_{n,m_1m_2}.) It follows that $d_{nn} = E_n + 1$. Presumably at low energies the discreteness of the tight binding model is irrelevant because of the long wavelengths of the eigenfunctions; similar issues have been discussed in ref. [32].

In flat space one must ultimately determine how a given distribution of line defects alters electronic states. Some insight is given by the following argument. We can write a single electron Schrödinger equation on a length scale large compared to the atomic spacing but small compared to the defect spacing

$$\left[-\frac{h^2}{2m}\nabla^2 + \Delta V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r}) \,, \tag{5.24}$$

where the deviation $\Delta V(\boldsymbol{r})$ of the potential from its mean value is caused by defects in the icosahedral ordering.

Following the Landau approach of sect. 3, we can relate the coarse grained potential $\Delta V(r)$ to the local order parameter $Q_{12,m_1m_2}(\boldsymbol{r})$. The deviation of particle density from its average value is

$$\rho(\boldsymbol{r}) - \rho_0 \equiv \Delta\rho(\boldsymbol{r}) \approx \sum_{m_1 m_2} Q_{12m_1m_2}(\boldsymbol{r}) Y^*_{12,m_1,m_2}(-1) \,, \tag{5.25}$$

where -1 is the point of tangency of the sphere in fig. 3. Using the relation (see eq. (2.8))

$$Y_{12,m_1m_2}(-1)=\sqrt{\frac{13}{2\pi^2}}\delta_{m_1m_2} \tag{5.26}$$

and assuming $\Delta V(\boldsymbol{r})$ is proportional to $\Delta\rho(\boldsymbol{r})$ we see that the Schrödinger equation is

$$\left[-\frac{h^2}{2m}\nabla^2+v_0\,\mathrm{Tr}\,\{Q_{12,m_1,m_2}(\boldsymbol{r})\}\right]\psi(\boldsymbol{r})=\varepsilon\psi(\boldsymbol{r})\,, \tag{5.27}$$

with v_0 a phenomenological constant. Because $Q_{12,m_1m_2}(\boldsymbol{r})$ vanishes on disclination lines, electrons are repelled from or attracted to these defects, depending on the sign of v_0.

It may also be of interest to solve nearly free electron models on S^3, with a weak potential which has the symmetries of polytope {3, 3, 5}. The relevant Schrödinger equation is

$$\left[-\frac{h^2}{2m}\nabla^2_{\hat{u}}+V(\hat{\boldsymbol{u}})\right]\psi(\hat{\boldsymbol{u}})=\varepsilon\psi(\hat{\boldsymbol{u}})\,, \tag{5.28}$$

where $\nabla^2_{\hat{u}}$ is the laplacian operator on S^3. The potential has the expansion

$$V(\hat{\boldsymbol{u}})=\sum_{n,m_1m_2}V_{n,m_1m_2}Y^*_{n,m_1m_2}(\hat{\boldsymbol{u}})\,, \tag{5.29}$$

where the only nonzero coefficients V_{n,m_1m_2} occur for the n-values listed in eq. (2.49). A description of energy bands in real metallic glasses would presumably require some combination of the tight binding and nearly-free electron methods discussed here.

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