

## Theory of the Structure Factor of Metallic Glasses

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A recently developed Landau description of short-range icosahedral order in supercooled liquids and metallic glasses is used to calculate density correlation functions in these systems. The theory predicts frustration-broadened peaks in the structure factor, at positions determined by the symmetries of an ideal, curved-space icosahedral crystal. The results provide a good fit to experiments on vapor-deposited metal films.

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A long-standing challenge in the theory of amorphous solids has been a direct theoretical understanding of scattering experiments which probe the structure of metallic glasses.<sup>1</sup> Despite relatively sharp peaks observed, e.g., in the structure factor  $S(q)$  of single-component vapor-deposited metal films,<sup>2,3</sup> conventional microcrystalline models do not appear tenable.<sup>4</sup>

There is mounting evidence that the short-range order in supercooled liquids and metallic glasses is predominantly icosahedral.<sup>5</sup> The growing icosahedral correlations found in molecular-dynamics simulations<sup>6</sup> are consistent with the rise in specific heat in undercooled liquid metals.<sup>7</sup> A number of authors<sup>8-10</sup> have argued that this icosahedral order is related to an ideal, icosahedral crystal (called "polytope {3,3,5}") consisting of 120 particles imbedded in the surface  $S^3$  of a four-dimensional (4D) sphere. Regions of short-range {3,3,5} order in a glass are broken up by a tangled array of  $-72^\circ$  wedge disclination lines, forced in by "frustration," i.e., the incompatibility of flat space with a space-filling icosahedral solid. The Frank-Kaspar phases of transition-metal alloys are ordered phases of these lines. A disordered network of such lines provides an appealing model for structure in metallic glasses.<sup>9</sup>

Recently, a uniformly frustrated Ginzburg-Landau free energy describing icosahedral order in dense liquids has been proposed.<sup>11</sup> A set of order parameters  $Q_{n,m_1,m_2}(\vec{r})$  is obtained by projecting a local particle configuration onto a 4D tangent sphere which can accommodate a perfect icosahedral lattice, and then expanding the projected particle density in the hyperspherical harmonics  $Y_{n,m_1,m_2}$ . These 4D spherical harmonics form a complete set of functions on the sphere  $S^3$ , and also generate irreducible representations of  $SO(4)$ ,  $n$  being the index of the representation. Only the representations  $n = 0, 12, 20, 24, 30, 32, 36, \dots$  are allowed for polytope {3,3,5}.<sup>11</sup> The azimuthal quantum numbers  $m_1$  and  $m_2$  vary in integer steps in the range

$-n/2 \leq m_1, m_2 \leq n/2$ . An earlier continuum elastic approach<sup>10</sup> used the  $n = 1$  representation of  $SO(4)$ , and did not allow explicitly for amplitude fluctuations. Because the magnitude of the order parameter vanishes at disclination cores, smooth variations in the order-parameter amplitude will in fact appear as soon as one uses coarse graining over a volume containing several disclinations. Since the disclination network forced in by the frustration is very dense,<sup>9</sup> amplitude fluctuations will be important at virtually all length scales, even at temperatures near  $T_g$ .

In this paper we use the Ginzburg-Landau theory to calculate density correlations in supercooled liquids and metallic glasses. The theory predicts a peak in the structure factor  $S(q)$  for every allowed value of  $n$ . A crude estimate of the peak position  $q_n$  is given by integrating the gradient squared of the relevant spherical harmonic over the unit vector  $\hat{u}$  parametrizing  $S^3$ ,<sup>11</sup>

$$q_n^2 \approx \kappa^2 \int d\Omega_{\hat{u}} |\nabla Y_{n,m_1,m_2}(\hat{u})|^2 = \kappa^2 n(n+2). \quad (1)$$

Here,  $\kappa$  is the inverse radius of the tangent sphere; it is related to the near-neighbor particle separation  $d$  in polytope {3,3,5} by<sup>9</sup>  $\kappa d = \pi/5 \approx 0.628$ . Our calculation makes these estimates precise, and shows explicitly how the peaks are broadened by frustration. The results are in good agreement with experiments on vapor-deposited metal films,<sup>2</sup> which exhibit peaks corresponding to  $n = 12, 20,$  and  $24$ , and an additional peak which appears to be a composite of  $n = 30$  and  $n = 32$ . The peaks in binary metallic glasses are broadened relative to single-component systems,<sup>1</sup> an effect which we show is easily accounted for with the Landau approach. We also remark on the relevance of these calculations to covalently bonded glasses.

Using the order parameters defined in Ref. 11, we can define a density on the tangent sphere at every point  $\vec{r}$  via the relation

$$\rho(\vec{r}, \hat{u}) = \sum_{n=0}^{\infty} \sum_{m_1, m_2} Q_{n,m_1,m_2}(\vec{r}) Y_{n,m_1,m_2}^*(\hat{u}).$$

The flat-space particle density  $\rho(\vec{r})$  is given by  $\rho(\vec{r}, -1)$ , where  $-1$  denotes the south pole of the tangent space. Since

$$Y_{n,m_1 m_2}(-1) = (-1)^n [(n+1)/2\pi^2]^{1/2} \delta_{m_1 m_2},$$

we see that the physical particle density is determined by the traces of the  $(n+1) \times (n+1)$ -matrix

$$F_n = \frac{1}{2} \int d^3 4 [K_n |(\partial_\mu - i\kappa \underline{L}_{0\mu}^{(n)}) \vec{Q}_n|^2 + r_n |\vec{Q}_n|^2] + O(Q^3). \quad (2)$$

For notational convenience, we have written the matrices  $Q_{n,m_1 m_2}$  as  $(n+1)^2$ -component vectors  $\vec{Q}_n$ . The form of the gradient term biases  $F_n$  toward neighboring particle configurations which are related by "rolling the sphere,"<sup>10</sup> or the equivalent "star mapping" construction of Sadoc and Mosseri.<sup>12</sup> The quantity  $\underline{L}_{0\mu}^{(n)}$  is a  $(n+1)^2 \times (n+1)^2$  matrix generator for rolling the  $n$ th representation of  $SO(4)$  in the direction  $\mu = x, y, \text{ or } z$ . The set of noncommuting matrices  $\{\kappa \underline{L}_{0\mu}^{(12)}, \kappa \underline{L}_{0\mu}^{(20)}, \dots\}$  play the role of reciprocal-lattice vectors in this approach.<sup>11</sup>

Our calculation is based on the following physical picture: When the masses  $r_n$  in Eq. (2) are positive, we have a high-temperature liquid, which can be regarded as a tangled mass of  $\pm 72^\circ$  disclination lines. At low temperatures, when the  $r_n$ 's are large and negative, the ground state is a Frank-Kasper lattice of  $-72^\circ$  disclination lines. We expect that  $r_{12}$ , the mass corresponding to the smallest reciprocal-lattice vector, changes sign at the mean-field instability temperature in  $S^3$  of an undercooled 120-particle liquid relative to the unfrustrated icosahedral crystal. In flat space, the frustration embodied in the gradient term in Eq. (2) will depress the corresponding instability temperature  $T_c^*$  against a Frank-Kasper phase down to very low temperatures. The situation is similar to the behavior near  $H_{c2}(t)$  of a type-II superconductor in a strong magnetic field,<sup>9</sup> except that the equilibrium

order parameters  $\{Q_{n,m_1 m_2}(r)\}$ . We shall impose the energetic preference for short-range icosahedral order by requiring that the total free energy be given by  $F = \sum_n F_n$ , with the summation restricted only to the icosahedral modes  $n = 12, 20, 24, \dots$ . We exclude, for simplicity, the unimportant uniform-density mode at  $n = 0$ . The free energy associated with the  $n$ th mode is given by<sup>11</sup>

transition to a Frank-Kasper disclination network (the analog of an Abrikosov flux lattice) is expected to be first order.<sup>11</sup>

The disclination lines in the high-temperature liquid carry non-Abelian  $SU(2)$  matrix charges. As a result, there are strong topological barriers inhibiting line crossings at low temperatures.<sup>9</sup> One would expect the kinetic constraints associated with this entanglement to increase with the amount of short-range icosahedral order, becoming more and more severe as a liquid is cooled below its freezing transition  $T_m$  to, say, an equilibrium fcc crystal. Good glass formers will drop out of equilibrium because of entanglement at a temperature  $T_g < T_m$  before reaching the instability temperature  $T_c^*$  against a Frank-Kasper phase.

These ideas suggest that we can evaluate density correlations in a glass (or in a liquid just above  $T_g$ ) by averaging over order-parameter configurations weighted by  $\exp(-F/k_B T_g)$ . As a first approximation, we can truncate the expansions in (2) at quadratic order in the  $\{\vec{Q}_n\}$ , since the large intrinsic density of defects forces these order parameters to be small. Note that we are using the statistical mechanics of a liquid in metastable equilibrium to determine preferred particle configurations, rather than a literal mapping<sup>8,12</sup> of polytope  $\{3,3,5\}$  into flat space.

The structure factor is given in terms of the Fourier-transformed particle density by

$$S(q) = \langle |\rho(\vec{q})|^2 \rangle = \sum_{n=12,20,24,\dots} \frac{n+1}{2\pi^2} \langle |\sum_m Q_{n,mm}(\vec{q})|^2 \rangle. \quad (3)$$

Upon Fourier transforming the free energy (2), we see that we need the eigenvalues and eigenvectors of  $\underline{Q}_n = q^2 - 2\kappa q_\mu \underline{L}_{0\mu}^{(n)} + \kappa^2 (\underline{L}_{0\mu}^{(n)})^2$ . The components of  $\underline{L}_{0\mu}^{(n)}$  can be evaluated by means of the homeomorphism between  $SO(4)$  and  $SU(2) \otimes SU(2)$ ,<sup>13</sup> and the noting that  $Q_{n,m_1 m_2}$  transforms like the composite angular momentum ket vector  $(-1)^{m_2} |\frac{1}{2}n, m_1, \frac{1}{2}n - m_2\rangle$ . After a simple unitary transformation, the generator  $\underline{L}_{0\mu}^{(n)}$  can be written as  $\underline{L}_{0\mu}^{(n)} = A_\mu^{(n/2)} - B_\mu^{(n/2)}$ , where  $A_\mu^{(n/2)}$  and  $B_\mu^{(n/2)}$

are the generators of two independent  $(n+1)$ -dimensional irreducible representations of  $SU(2)$ .

The problem of diagonalizing the  $\underline{Q}_n$ 's is simplified by first noting that the operator  $\hat{M}_n = \hat{q} \cdot [\vec{A}^{(n/2)} + \vec{B}^{(n/2)}]$  commutes with  $\underline{Q}_n$ , and has integral eigenvalues in the range  $-n \leq M \leq n$ . Quantizing along the  $\hat{q}$  axis, we find that  $\underline{Q}_n$  breaks into  $(n - |M| + 1)$ -dimensional subspaces indexed by the value of  $M$ . It follows that we can denote

the eigenvalues of  $\underline{\mathcal{D}}_n$  by  $\lambda_{M,i}^n$ , where  $i$  runs from  $i$  to  $n - |M| + 1$ . The result of numerically determining the lowest three eigenvalues in each subspace for  $n = 12$  as a function of  $|\bar{q}|$  is shown in Fig. 1. The eigenvalues for  $+M$  and  $-M$  are degenerate. The fact that these eigenvalues are always positive is due to the frustration embodied in Eq. (2); it is impossible to make the gradient term vanish everywhere.<sup>11</sup> Because  $Q_{n,mm} \sim |\frac{1}{2}n m, \frac{1}{2}n - m\rangle$ , only the eigenvalues of the  $M = 0$  manifold will contribute to the structure function. It follows from Eq. (3) and the equipartition theorem that

$$S(q) = \sum_{n=12,20,24,\dots} \frac{n+1}{2\pi^2} \sum_i \frac{k_B T_g}{K_n \lambda_{0,i}^n(q) + r_n} |\sum_m e_{n,mm}^i|^2,$$

where  $e_{n,mm}^i$  is the projection of the  $i$ th eigenvector onto  $Q_{n,mm}$ . Evidently, there will be for every  $n$ , a peak in  $S(q)$  which is essentially determined by the wave vector  $q_{\min}$  minimizing the smallest  $M=0$  eigenvalue,  $\lambda_{0,i}^n(q)$ . Both numerical and perturbative evaluations of  $q_{\min}$  are consistent with the estimate in Eq. (1).

The theory formulated above is directly applicable to monatomic metallic glasses. While it has not yet been experimentally possible to make such substances by spin-cooling the melt, one can make thin films of amorphous metals by vapor deposition onto a cold substrate. It is believed that essentially the same structure would result if one could cool the melt fast enough.<sup>4</sup> Figure 2 shows a fit of our results to the measurements of Leung and Wright<sup>3</sup> on amorphous cobalt. Two parameters,  $K_n/k_B T_g$  and  $r_n/k_B T_g$ , have been adjusted for each peak. The peak positions  $q_n$ , however, are completely determined by the theory once  $\kappa$  is known: We find that  $q_{12} = 11.25\kappa$ ,  $q_{20} = 19.20\kappa$ , and  $q_{24} = 22.96\kappa$ . The value of  $\kappa$  was obtained from the main position of the first peak. Using the relation  $\kappa d = \pi/5$ , we obtain a particle spacing  $d$  on the polytope which is approximately 10% less than the position of the first peak in the flat-space radial distribution function. The theoretical value for the ra-

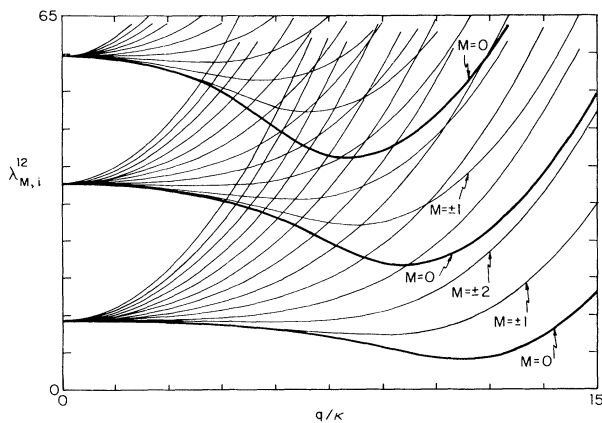


FIG. 1. A plot of the lowest three eigenvalues for all  $M$  of  $\underline{\mathcal{D}}_{12}$ . Heavy lines correspond to the  $M = 0$  manifold.

tio  $q_{20}/q_{12}$  is 1% higher than the experimental result  $q_{20}/q_{12} = 1.69$ , while the ratio  $q_{24}/q_{12}$  exceeds by 3.6% the experimental value  $q_{24}/q_{12} = 1.97$ . The  $n = 30$  and  $n = 32$  peaks are quite close together, and appear as a single peak in the experiment. The fits determine a set of masses  $r_{12}, r_{20}, r_{24}, \dots$  which are all negative, consistent with the physical picture discussed above. The free energy is stabilized, despite these negative masses, by the frustration. An estimate of the effect of the nonlinear terms in Eq. (3) shows that the  $n = 24$  peak is shifted closer to the experimentally observed position, with much smaller shifts in the remaining peaks. Because the peaks for large  $n$  correspond to large reciprocal-lattice vectors (i.e., closely spaced Bragg planes), we expect that they will be broadened more by frustration.

Two-component metallic glasses can be incorporated into the theory when we allow for an additional fluctuating impurity concentration  $c(\bar{r})$ . The simplest way in which this composition can couple to the order parameter (other than changing

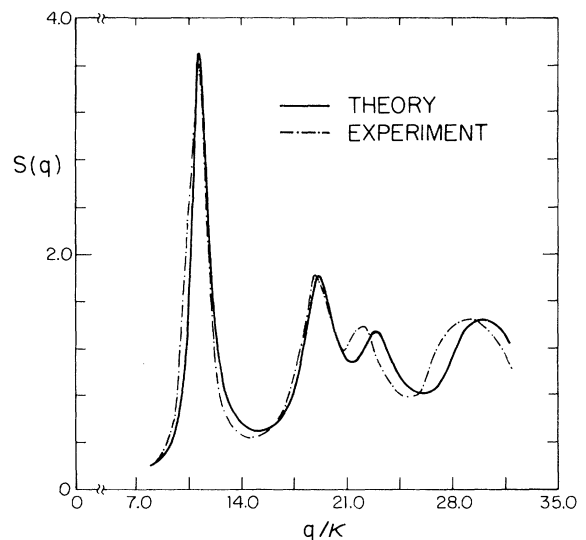


FIG. 2. Theoretical fit to the structure function of amorphous cobalt (Ref. 3). Peak heights and widths determine parameters in the Landau expansion; the peak positions are a consequence of the theory.

$\kappa$ ) is via the replacement

$$F \rightarrow F + \int d^3r \left( \sum_{n=12,20,24,\dots} \gamma_n c |\bar{Q}_n|^2 + \frac{1}{2} \chi^{-1} c^2 - c \Delta \right),$$

where  $\chi$  is the concentration susceptibility, the  $\gamma_n$  are coupling constants, and  $\Delta$  is an impurity chemical potential. It is straightforward to show that the effect of this coupling is to broaden the peaks in pure systems, without significantly changing their relative positions. This seems to be what is observed experimentally.<sup>1</sup>

It may be possible to apply these ideas to covalently bonded glasses as well. Although the energetic arguments are less well founded than for metallic glasses,<sup>5</sup> one appealing candidate for describing tetrahedrally coordinated glasses is "polytope 240,"<sup>12</sup> which is a regular lattice of boat-shaped rings inscribed on  $S^3$ . Particle configurations with short-range polytope-240 order are also characterized by nonzero hyperspherical harmonics with  $n = 12, 20, 24, \dots$ . This polytope should be especially appropriate for III-V compound semiconductors.<sup>14</sup> One complication, however, is that there are actually two chiral variants of polytope 240.<sup>15</sup> Thus one might expect the short-range order to be disrupted by domain walls separating regions of different chirality, as well as by disclination lines. A more detailed account of these calculations will appear in a future publication.

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