

## Frustration and Curvature: Glasses and the Cholesteric Blue Phase

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An analogy is drawn between continuum elastic theories of the blue phase of cholesteric liquid crystals and recent theories of frustration in configurational glasses. Both involve the introduction of a lattice of disclination lines to relieve frustration; the frustration is due to an intrinsic curvature in the natural form of parallel transport. A continuum theory of configurational glasses is proposed.

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According to current models,<sup>1</sup> glasses are characterized by having potential-energy functions with many local minima. In spin-glasses, disorder is not sufficient to provide glassy behavior; the importance of frustration<sup>2</sup> in breaking ergodicity and providing multiple metastable ground states has long been recognized. Recently, several authors have proposed<sup>3</sup> that a kind of frustration is important in describing configurational glasses. They describe a short-range order in liquids and glasses that is incompatible with crystallinity; they view the substance as a conglomeration of local low-energy structures separated by regions of high strain.

For example, many models of metallic glasses are frustrated because the natural tetrahedral cluster cannot be used to tile space. The liquid and glassy states have local icosahedral order; this local low-energy icosahedral cluster gives way in the equilibrium low-temperature phase to long-range crystalline order (e.g., fcc or hcp). This description bears a striking similarity to that of cholesteric liquid crystals.<sup>4</sup> Here the local low-energy "double twist" tubes characteristic of the blue phases cannot fill space without introducing defect lines. At low temperatures the blue phases give way to the defect-free cholesteric spiral phase, which twists only in one direction.

Curvature has been used to describe this frustration. Although the local low-energy configuration is frustrated from filling physical space, in both these examples it can be extended into an unfrustrated texture on a sphere  $S^3$  in four dimensions. For the metallic glasses,<sup>5</sup> 120 atoms form 600 tetrahedra on a sphere of radius  $\kappa^{-1} = 1.59 \dots$  times the interparticle spacing; five tetrahedra meet at each edge. For the blue phase,<sup>6</sup> a director field

$$\vec{n} = q(-X_1, X_0, X_3, -X_2) \quad (1)$$

on a sphere with circumference the cholesteric pitch  $P = 2\pi/q$  everywhere satisfies the double-twist condition. Thus  $q$  for cholesteric liquid crystals is analogous to  $\kappa$  in metallic glasses. In this paper we shall use these textures on  $S^3$  as templates of an ideal ordering in curved space to define and study the frustrated glassy state in physical space.

We take the standard definition of the order parameter used in topological theories of dislocations and disclinations in crystalline material.<sup>7</sup> We describe the nonuniform medium at a point  $\vec{r}$  in physical space by looking for the local configuration in the texture on  $S^3$  which most closely resembles the immediate environment of  $\vec{r}$ . For example, in Fig. 1 the order parameter is given by a point  $p$  in the pentagonal unit cell of the ideal structure, together with a rotation orienting the pentagon containing  $p$  with the distorted pentagon containing  $\vec{r}$ . The order parameter  $\Sigma(\vec{r})$  is fully specified by a rigid-body rotation  $\tilde{\Sigma} \in \text{SO}(4)$  of  $S^3$  which aligns the two configurations. Let latin indices run from 1 to 3, and Greek

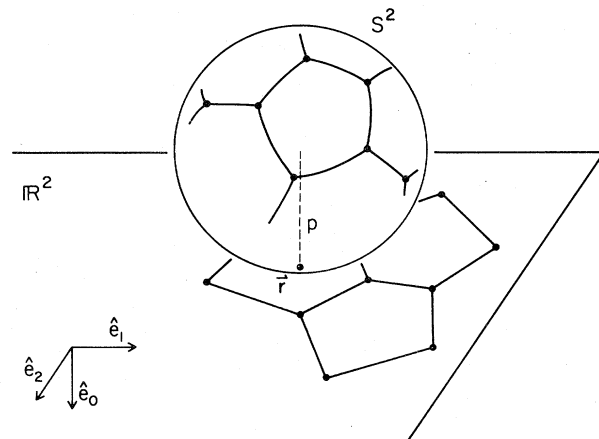


FIG. 1. Ideal texture on the sphere projects onto the local low-energy structure in physical space.

indices from 0 to 3. Let  $\hat{x}_0 = (\kappa^{-1}, 0, 0, 0)$  be the point on  $S^3$  tangent to  $R^3$ . Then  $\hat{p}(r) = [\tilde{\Sigma}(r)]^{-1}(\hat{x}_0)$ , so that  $\hat{p}_\nu = \kappa^{-1}\Sigma_{0\nu}$  describes the translational order within a unit cell. The other components  $\tilde{\Sigma}_{j\nu}$  describe the orientational order—the relative alignment of the ideal unit cell and the real one.

However, the local configuration near  $\vec{r}$  need not uniquely specify a rotation. Two rotations  $\tilde{\Sigma}_1$  and  $\tilde{\Sigma}_2$  will define the same configuration if  $g = \tilde{\Sigma}_1^{-1}\tilde{\Sigma}_2$  is a symmetry of the ideal texture. Thus if  $G$  is the symmetry group of the texture, the order parameter is an equivalence class  $\Sigma = \{\tilde{\Sigma}g, g \in G\}$ ; it is contained in the right coset space  $SO(4)/G$ .

The symmetry group of the 120-atom metallic-glass texture is discrete. It describes the allowed disclination lines, but does not change the local differential structure of the order parameter. For the present purposes, we will continue to treat  $\Sigma$  for metallic glasses as a rotation of  $S^3$ . On the other hand, the blue-phase texture [Eq. (1)] has a continuous symmetry group. A rotation  $\tilde{\Sigma}$  preserves  $\vec{n}$  if  $\vec{n}(\vec{x}) = \tilde{\Sigma}\vec{n}(\tilde{\Sigma}^{-1}\vec{x})$ ; if  $\tilde{\Sigma}$  is infinitesimal  $\tilde{\Sigma} = 1 + \epsilon J$ , this implies  $[J, \partial n] = 0$ . In the six-dimensional space of infinitesimal rotations, a four-dimensional subspace satisfies this condition. A straightforward computation shows that the order-parameter space  $SO(4)/G$  is the space  $RP^2$  of directors (headless vectors). Thus, at the risk of some confusion, we shall use  $n$  to represent the blue-phase order parameter.

A topological theory is sufficient to classify defects, but to study frustration one must have a differential structure. To write down elastic free energies, we need a notion of parallel transport. Clearly, a low-energy configuration will be a projection of a segment of the sphere  $S^3$  onto physical space  $R^3$  (see Fig. 1). The natural definition of parallel transport thus amounts to rolling the sphere. (This was noted by Kléman and Sadoc.<sup>5</sup>) That is  $\Sigma(\vec{x} + \vec{\delta})$  is "parallel" to  $\Sigma(\vec{x})$  if  $\Sigma(x + \delta) = R_\delta \Sigma(x)$ , where  $R_\delta$  is the rotation matrix in  $SO(4)$  which rolls the sphere the distance  $\vec{\delta}$ . Let  $\hat{e}_1, \hat{e}_2, \hat{e}_3$  be a basis for  $R^3$  and  $\hat{e}_0$  be the formal direction perpendicular to it. Then the infinitesimal generator  $J_i$  for rolling the sphere in the  $\hat{e}_i$  direction is  $J_{i\mu\nu} = \delta_{0\mu}\delta_{i\nu} - \delta_{i\mu}\delta_{0\nu}$ ;  $R_{\delta e_i} = \exp(\delta \kappa J_i)$ . The covariant deriva-

tive is therefore

$$(D_i \Sigma)_{\mu\nu} = \lim_{\delta \rightarrow 0} \frac{[\Sigma(x + \delta \hat{e}_i)] [R_{\delta e_i} \Sigma(x)]^{-1} - 1}{\delta} \\ = (\partial_i \Sigma)_{\mu\rho} \Sigma_{\nu\rho} - \kappa J_{i\mu\nu}. \quad (2)$$

This construction also defines parallel transport when the texture has a continuous symmetry. This follows mathematically since the covariant derivative acts on the left, while the symmetry group acts on the right. If  $\tilde{\Sigma}_1 = \tilde{\Sigma}_2 g$  for  $g \in G$ , then  $R_\delta \tilde{\Sigma}_1 = (R_\delta \tilde{\Sigma}_2)g$ , so that parallel transport respects right cosets. Physically, this conclusion is obvious—the projection onto physical space of a local neighborhood on  $S^3$  will not change if we rotate  $S^3$  preserving the texture. Expressed in terms of the director  $\vec{n}$ , the covariant derivative defined by the blue-phase texture is

$$(\tilde{D}_i n)_j = \partial_i n_j + q \epsilon_{ijk} n_k \quad (3)$$

which reflects the desire of the cholesteric fluid to twist in both directions perpendicular to the local axis.

Both covariant derivatives  $D$  and  $\tilde{D}$  are frustrated; they cannot be made to vanish in flat physical space. This frustration is embodied in the curvature tensors constructed from  $D$  and  $\tilde{D}$ . The curvature tensor expresses the change in the order parameter under parallel transport about a closed loop. Only if it vanishes can one have an order-parameter field whose covariant derivative vanishes everywhere. If one transports  $\Sigma$  a distance  $\delta$  in turn along the  $\hat{e}_i, \hat{e}_j, -\hat{e}_i,$  and  $-\hat{e}_j$  directions it will change to  $\Sigma - \delta^2 \kappa^2 [J_i, J_j] \Sigma$ ; thus the curvature tensor for  $D$  is

$$R_{\mu\nu ij} = \kappa^2 [J_i, J_j]_{\mu\nu} = \kappa^2 (\delta_{j\mu} \delta_{i\nu} - \delta_{i\mu} \delta_{j\nu}). \quad (4)$$

Since  $\vec{n}$  transforms like a vector, its parallel transport is described by traditional differential geometry. [ $\tilde{D}$  is an affine connection on the tangent bundle, while  $D$  is a connection on a fiber bundle with structure group  $SO(4)$ .] Its curvature tensor

$$\tilde{R}_{ijkl} = q^2 (\delta_{il} \delta_{kj} - \delta_{ik} \delta_{lj}) \quad (5)$$

can be contracted to form a scalar curvature

$$\tilde{R}_{ij ij} = -6q^2 \quad (6)$$

which is negative.<sup>8</sup>

The elastic theory of the blue phase has been pursued in some detail.<sup>4,9</sup> A sensible form for the gradient terms in the cholesteric free energy (the "one constant approximation") can be expressed in terms of the covariant derivative  $\tilde{D}$ :

$$\tilde{F}_{\text{grad}} \{ \vec{n} \} = \frac{1}{2} K n^2 (\tilde{D}n)^2 = \frac{1}{2} K \{ n^2 (\text{div } n)^2 + (n \times \text{curl } n)^2 + (n \cdot \text{curl } n + qn^2)^2 \} \\ + \frac{1}{2} K n^2 \text{div} \{ \frac{1}{2} \text{grad}(n^2) - n \times \text{curl } n - n \text{div } n \} + \frac{1}{2} K q^2 n^4. \quad (7)$$

For fixed  $|n|=1$  this is the traditional Frank elastic free energy for cholesterics, plus a total divergence.

The blue phases lie in a small temperature band between the cholesteric planar spiral phase and the isotropic melted state. At least two of these blue phases are lattices of low-energy double-twist regions, separated by lattices of disclination lines. These structures are formed by cutting open and flattening the ideal texture on  $S^3$ , adding wedges of new material to ease the strains. The  $S=-\frac{1}{2}$  disclination lines are the terminating edges of these cuts. To allow an isotropic core to form around the defect lines, I have let  $\vec{n}$  vary in magnitude in Eq. (7). In the blue phases, this core size is a reasonable fraction of the distance between defect lines.

In the blue phase, the curvature length scale  $q^{-1} \sim 1000 \text{ \AA}$  is large compared to the molecular length. As noted earlier, in metallic glasses these two length scales are the same. If current speculations are correct<sup>5</sup> that this curvature is central to the behavior of metallic glasses, then perhaps a theory in which the molecular length is formally made small will facilitate analysis while retaining the important physics. In analogy with Eq. (7), we can form a continuum elastic free energy for metallic glasses proportional to  $(D\Sigma)^2$ :

$$F_{\text{grad}}(\Sigma) \propto (D_i \Sigma)_{\mu\nu} (D_i \Sigma)_{\mu\nu}. \quad (8)$$

I imagine partitioning the volume between the metal atoms into tetrahedra, and filling each by stretching and flattening one of the 600 tetrahedral segments of the sphere.  $F_{\text{grad}}$  gives precisely the linear elastic energy needed to deform the tetrahedra.<sup>10</sup> Although not a pair potential, it provides a legitimate interaction energy for the original metal atoms, embodying in a direct way the curvature-induced frustration.

We have constructed a frustrated continuum elastic theory for metallic glasses.<sup>11</sup> A strict analogy with the blue phase has been demonstrated, by reconstructing a well accepted elastic theory of cholesteric liquids using exactly the same procedure. Experimentally, between the two crystalline blue phase and the isotropic fluid state there often occurs a thermodynamically stable, amorphous "blue fog" state. If the metallic free energy also can have an amorphous ground state, one must hope that it will possess the (presumed) universal features of the glass-liquid transition. For example, if there is a phase transition in this model with three as a

lower critical dimension, essential singularities similar to those in the Kondo problem and in the Kosterlitz-Thouless transition might be found.

P. W. Anderson first described the blue phase in terms of a covariant derivative. I would like to thank him, David Ellis, David Mermin, David Wright, David Nelson, Stuart Trugman, Eric Siggia, Nick Manton, Eduardo Fradkin, and Maurice Kléman for helpful conversations, and the Aspen Center for Physics for hospitality during the final stages of this work. This work was supported in part by the National Science Foundation through Grants No. DMR 802063, No. ATM 80-05796, and No. PHY 77-27084 (supplemented by funds from the National Aeronautics and Space Administration).

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<sup>4</sup>S. Meiboom, J. P. Sethna, P. W. Anderson, and W. F. Brinkman, *Phys. Rev. Lett.* **46**, 1216 (1981); R. M. Hornreich, M. Kugler, and S. Shtrikman, *Phys. Rev. Lett.* **48**, 1404 (1982); S. Meiboom, M. Sammon, and W. F. Brinkman, *Phys. Rev. A* **27**, 438 (1983). In analogy with these blue-phase theories, M. Kléman [*J. Phys.* **43**, 1389 (1982)] has tried to describe metallic glasses in terms of tubes.

<sup>5</sup>M. Kléman and J. F. Sadoc, *J. Phys. (Paris), Lett.* **40**, L569 (1979), and later publications; D. R. Nelson, *Phys. Rev. Lett.* **50**, 982 (1983), and to be published. Related ideas were discussed by N. Rivier, *Philos. Mag. A* **40**, 859 (1979).

<sup>6</sup>J. P. Sethna, D. C. Wright, and N. D. Mermin, *Phys. Rev. Lett.* **51**, 467 (1983).

<sup>7</sup>N. D. Mermin, *Rev. Mod. Phys.* **51**, 591 (1979).

<sup>8</sup>The use of the word curvature in this context is often confusing. The curvature of a covariant derivative which is compatible with the metric agrees with the curvature of the underlying space if the torsion vanishes [N. J. Hicks, *Notes on Differential Geometry* (Van

Nostrand, Princeton, 1965), pp. 64 ff]. The torsion of  $\tilde{D}$  is  $\tilde{T}_{ijk} = q\epsilon_{ijk}$ . E. Schrödinger discusses torsion in *Space-Time Structure* (Cambridge Univ. Press, Cambridge, 1950), Chap. 5. S. Kobayashi and K. Nomizu, *Foundations of Differential Geometry* (Interscience, New York, 1969), is a standard reference on fiber bundles.

<sup>9</sup>S. A. Brazovskii and S. G. Dmitriev, Zh. Eksp. Teor. Fiz. **69**, 979 (1975) [Sov. Phys. JETP **42**, 497 (1975)]; R. M. Hornreich and S. Shtrikman, J. Phys. (Paris) **41**, 335 (1980), and Phys. Lett. **84A**, 20 (1981).

<sup>10</sup>More general free energies can be formed with other quadratic scalar contractions of  $D$  and  $\tilde{D}$ . In the blue phase,  $\tilde{F}_{\text{grad}}$  can contain terms of the form  $(\tilde{D}_i n)_i^2$  and  $(\tilde{D}_i n)_j (\tilde{D}_j n)_i$ . Even with these terms,  $\tilde{F}_{\text{grad}}$  is not the most general director free energy (D. Wright, to be published); not every frustrated free energy can be written in terms of a covariant derivative.

In the metallic glasses, the point of tangency  $x_0$  can be used to form free energies which distinguish translational and orientational order. In particular,  $\kappa^{-1}(D_i \Sigma)_{0j} = (\partial_i p_\nu) \Sigma_{j\nu} - \delta_{ij} = \sigma_{ij}$  is analogous to the strain tensor in traditional elasticity, so that  $F_{\text{grad}}^*(\Sigma) = 2\mu \sigma_{ij} \sigma_{ij} + \lambda (\sigma_{ii})^2$  is the naive generalization of isotropic flat-space continuum elastic theory. However, the curvature  $R_{0\nu ij} = 0$ ; although  $F^*$  is presumably still frustrated, the frustration can only occur at higher order.

In principle, the map  $p(\gamma)$  specifies completely the physical state in real space; the components  $\Sigma_{j\nu}$  are extra degrees of freedom introduced to simplify the algebra. Mermin (Ref. 7) has expressed qualms about the topological effects of these artificial modes. Here the free energy should act to enslave these degrees of freedom to gradients of  $p$ .

$F_{\text{grad}}$  contains gradients of  $\Sigma_{j\nu}$ , and thus implicitly second derivatives of  $p$ . In normal elastic theory second derivatives are higher order in the lattice constant over the wavelength, and are dropped. Our lattice constant is not small, and we are justified in keeping whatever higher-order gradients appear important. The extra terms in  $F$  not contained in  $F^*$  are qualitatively necessary to maintain the curvature-induced frustration. Thus I believe that  $F$  of Eq. (8) is the correct continuum model for metallic glasses.

<sup>11</sup>One might hope to construct a continuum theory by looking only at orientational order [using  $\text{SO}(3)$  rather than  $\text{SO}(4)$  as an order parameter]. That is, instead of filling in between the atoms, one imposes a cutoff length large compared to the lattice constant, ignoring the translational degrees of freedom (see, e.g., D. Nelson, to be published). This works, for example, in two-dimensional melting because the ideal structure is planar, and translations form a subgroup of the automorphisms of the plane. The automorphism group  $\text{SO}(4)$  of the sphere naturally splits into left and right rotations  $\text{SO}_R(3) \otimes \text{SO}_L(3)$ , but this splitting is chiral and leads to blue phases.

It is easy to see that any connection on  $\text{SO}(3)$  over  $R^3$  leads to an affine connection which is compatible with the metric. For the curvature to be nonzero, the connection must have torsion (Ref. 8). Thus it would seem that any frustrated theory of this type using  $\text{SO}(3)$  as an order parameter will be chiral. A theory of metallic glasses using  $\text{SO}(3)$  as an order parameter must construct an affine connection on flat space compatible with the metric whose gauge invariants (such as the curvature) are isotropic, homogeneous, and nonchiral. This does not seem to be possible.