Quantization Rules for Point Singularities in Superfluid ^{3}He and Liquid Crystals*

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I show that pointlike singularities can exist in superfluid ^{3}He. Integer quantum numbers are associated with these singularities. The quantization rules follow from the single valuedness of the order parameter and quantities derived from it. The results are also easily extended to the quantization of point singularities in nematic liquid crystals. The pointlike singularities in ^{3}He-A are experimentally accessible analogs of the magnetic monopole.

The quantization of vortices in superfluid ^{4}He and in superconductors is a consequence of the existence of a single-valued complex order parameter, $\psi = |\psi| \exp i\varphi$. The single-valuedness assumption implies that the phase, φ, can only change by an integral multiple of 2π upon traversing any closed path in coordinate space so that

$$\oint \nabla\varphi \cdot d\vec{L} = 2\pi N. \tag{1}$$

As a result, circulation and fluxoid are quantized in the respective cases.

I shall show that similar considerations lead to the quantization of pointlike singularities (which I call vortons for brevity), occurring in vector fields derived from the (tensorial) order parameter of superfluid ^{3}He. Since the quantization rule only requires a well-defined vector field, it may be applied in other contexts, e.g., to the director field in nematic liquid crystals.

I will derive the quantization rule within the framework of one of the physically more interesting cases: a complex order parameter which appears to describe ^{3}He-A and has the form

$$\psi(\vec{r}_1, \vec{r}_2) = \chi(\vec{R})\vec{R}\cdot[\hat{\Delta}_1(\vec{r}) + i\hat{\Delta}_2(\vec{r})], \tag{2}$$

where $\vec{r} = (\vec{r}_1 + \vec{r}_2)/2$, $\vec{R} = \vec{r}_1 - \vec{r}_2$, $\hat{\Delta}_a \cdot \hat{\Delta}_b = \delta_{ab}$, and where the local symmetry axis is given by $\hat{l} = \hat{\Delta}_1 \times \hat{\Delta}_2$. $\hat{l}$ is particularly appropriate for application of the quantization rule because, besides the possibility of "real" vortons, it can also be manipulated (by the choice of boundary of the ^{3}He-A sample and by the creation of a multiply connected sample through seeding the sample with particles of foreign matter) to give nontrivial examples (i.e., quantum numbers not equal to zero) of the quantization rule. This results from the apparent tendency of $\hat{l}$ to orient itself perpendicular to boundaries.[1]

Reserving upper indices for the components of $\hat{\Delta}_1$, $\hat{\Delta}_2$, and $\hat{l}$, I define

$$l_i{}^a = \partial l^a/\partial x_i, \tag{3}$$

and will prove that

$$N = \frac{1}{8\pi}\int d^3x\, \epsilon_{ijk}\,\epsilon_{abc}\, l_i{}^a l_j{}^b l_k{}^c \tag{4}$$

is an integer if $\hat{l}$ is a single-valued vector field and $\hat{l}\cdot\hat{l} = 1$, where ϵ_{ijk} is the usual antisymmetric tensor with $\epsilon_{123} = 1$, $\epsilon_{132} = -1$, etc. The integrand of Eq. (4) will also be shown to be zero except for vortons where δ-function singularities occur.

I now prove that N is an integer. First note that (4) may be rewritten as a surface integral

$$N = \frac{1}{8\pi}\int_s d\vec{s}\cdot\vec{u}, \tag{5}$$

where

$$u_i = \epsilon_{ijk}\,\epsilon_{abc}\, l^a l_j{}^b l_k{}^c, \tag{6}$$

and where, without loss of generality, I take the surface to be a sphere. I parametrize the surface with two variables, η_1 and η_2, so that

$$dS_i = \frac{1}{2}\epsilon_{ijk}\frac{\partial(x_j, x_k)}{\partial(\eta_1, \eta_2)}\, d^2\eta. \tag{7}$$

After expressing the derivatives of $\hat{l}$ in terms of derivatives with respect to the new variables,

$$l_j{}^a = \frac{\partial\eta_p}{\partial x_j}\frac{\partial l^a}{\partial\eta_p}, \tag{8}$$

I find

$$N = \frac{1}{4\pi}\int d^2\eta\, \hat{l}\cdot\vec{n}, \tag{9}$$

where

$$\vec{n} = \frac{1}{2}\epsilon_{abc}\frac{\partial(l^b, l^c)}{\partial(\eta_1, \eta_2)}. \tag{10}$$

From Eq. (10) we see that $\vec{n}$ is the normal to the surface $\hat{l}\cdot\hat{l} = 1$ and thus the integral in Eq. (9) gives the area of the unit $\hat{l}$ sphere[2] multiplied by the difference of the number of times the area of the unit $\hat{l}$ sphere is swept out in a positive sense minus the number of times the area is swept out in a negative sense as I cover the sphere parametrized by η_1 and η_2 in coordinate space. The single valuedness of $\hat{l}$ implies that the difference must be an integer and thus N is a positive or negative integer.

The quantization rule can be rewritten in terms of the more fundamental fields, $\hat{\Delta}_i$, by substitution of $\hat{l}=\hat{\Delta}_1\times\hat{\Delta}_2$ in Eq. (5) with the result

$$\vec{u}=2\nabla\times\vec{v}, \tag{11}$$

where

$$\vec{v}=\Delta_1{}^a\nabla\Delta_2{}^a, \tag{12}$$

with repeated indices summed. Equation (11) proves that the integrand in Eq. (4) is zero except for a set of points of measure zero. Furthermore, it also reveals, by comparison with Eq. (6) of Mermin and Ho,[3]

$$(\nabla\times\vec{v}_s)_i=\frac{\hbar}{2M}\epsilon_{ijk}\epsilon_{abc}l^a l_j{}^b l_k{}^c \tag{13}$$

(with $\vec{v}_s$ usually identified as the ^{3}He-A superfluid velocity field), that

$$\vec{v}=(M/\hbar)\vec{v}_s, \tag{14}$$

up to an irrelevant gradiant term. Use of Stokes's theorem relates N directly to $\vec{v}_s$,

$$N=(M/2h)\oint d\vec{L}\cdot\vec{v}_s, \tag{15}$$

and betrays a striking similarity in form to the circulation quantization condition in superfluid ^{4}He. The line integral in Eq. (15) encloses *only* the singular points of $\vec{v}_s$ in the surface S and usually must be obtained as the limit of another contour shrunk to enclose only singular points.

If we apply the above considerations to a unit vorton at the origin, $\hat{l}=\hat{r}$, then we find the integrand of Eq. (4) is $8\pi\delta^3(\vec{r})$ giving $N=1$. A possible $\vec{v}_s$ field associated with the unit vorton has singularities at $\theta=0$ and $\theta=\pi$ (in a spherical coordinate system established for simplicity on a unit sphere in r space) and the line integral in Eq. (15) consists of two circles on the sphere, one around each singularity, which are (after integration) shrunk to enclose just the two singular points. The contributions from each singularity are equal and add to give $N=1$.

The discussion of quantized structures in superfluid ^{3}He has depended only on the existence of single-valued vector functions associated with the order-parameter tensor. This reflects the underlying basis of the quantization of vortons in homotopy theory.[4] The quantum number, N, is equal to the Brouwer degree of the vorton. Thus the integral nature of N is a consequence of the topological structure of three functions defined on a three-dimensional coordinate space and does not depend on dynamical considerations. As a result, the quantization rule, Eq. (4), can be relevant in other contexts where a single-valued function is defined, and can be extended to cases with multivalued vector fields. A case in point is nematic liquid crystals where the director field, $\vec{d}$, is double valued in the sense that $\vec{d}$ and $-\vec{d}$ describe the same physical situation. A choice of direction for $\vec{d}$ at one point in a sample and the requirement of continuity given a unique determination of the director field at all points of the sample with the possible exception of two-dimensional surfaces where $\vec{d}$ is undefined. Then the quantization rule, Eq. (4), can be used without modification to classify point singularities, which have been observed experimentally.[5] The new features resulting from the ambiguity in $\vec{d}$'s direction are (i) N may now be half-integral as well as integral,[6] and (ii) the sign of N is arbitrary as can be seen by letting $\vec{d}\to-\vec{d}$ in the quantization rule. An interesting class of unit director fields is given in Rer. 5, $\hat{d}=(\sin A\cos B,\ \sin A\sin B,\ \cos A)$ where $B=|N|\varphi$ and

$$A=2\arctan\{[\tan(\theta/2)]^{|N|}\}, \tag{16}$$

with θ and φ the usual spherical angles. A singularity exists at the origin with quantum number $|N|$.

In conclusion I have found that the additional degrees of freedom in superfluid ^{3}He lead to the possibility of pointlike singularities, vortons, in addition to the previously conjectured linear singularity structures, vortices and disgyrations.[7] Vortons are quantized and are the endpoints of one or more vortex lines in $\vec{v}_s$. [By Eq. (15) we know that any surface enclosing a vorton has at least one point where $\vec{v}_s$ is singular which implies, by continuity, the existence of singular $\vec{v}_s$ lines emanating from a vorton.] An analogy can be made between vortons and magnetic monopoles with the Dirac string[8] being the analog of a vortex emanating from a vorton. In the case of the 't Hooft model of the magnetic monopole, the magnetic charge[3] is a topological quantum number just as Eq. (4). Thus the study of vortons would appear to be of wide interest.

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Crystal-Field Effects and the Migration of Transition-Metal Ions in AgCl†

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The diffusion of a set of consecutive divalent transition-metal ions has been measured in AgCl. Their high-temperature activation energies are found to span the range from 1 to 2 eV and to exhibit a systematic dependence on the number of electrons in the d shell. The relative migration energies can be quantitatively accounted for in terms of the electronic contributions to the energies of the ions, in the normal and activated positions, resulting from crystal-field splittings.

An understanding of the properties of impurity ions in ion crystals, such as the silver halides, requires a consideration of the effect of the crystalline field on the electronic states of these ions. In this Letter, this effect is shown to be reflected in the activation energies for the substitutional migration of the first-row transition elements in silver chloride. Although these notions have been previously used in interpreting the partitioning of transition elements in duplex scales on oxidized alloys,[1] the present results are believed to demonstrate clearly, for the first time, a quantitative correlation between an ion transport phenomenon and the effects of the crystal field at the various sites in a simple halide salt.

The activation energies for diffusion in AgCl of V^{2+}, Cr^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} (all $3d^n$ ions) have been determined from the temperature dependence of the diffusion coefficient as measured by the conventional tracer-sectioning technique.[2] (The details of the measurements will be given elsewhere.) These energies, along with those previously reported for the diffusion of divalent manganese[3] and zinc,[4] are presented in Table I. Only the values derived from least-squares fits to the high-temperature data are shown since the values in that range may be taken to be insensitive to the codiffusion of polyvalent impurities in the tracer solution and to residual impurities in the host crystal, and thus are deemed as quite accurate for the purpose of comparison. It may be noted that the temperature range for the Ni^{2+} measurements is small; this is due to the less-sensitive surface counting method required by the

TABLE I. Diffusion of first-row transition-metal ions in AgCl.

Tracer	Configuration	Temperature range (°C)	Diffusion activation energy (eV)	$H_m^{\text{solute}} - H_m^{\text{Mn}^{2+}}$ (eV) Expt. (± 0.03 eV)	Avg. calc.	Individual ion calc.
V^{2+}	$3d^3$	352–441	2.08	0.90	0.88	0.96
Cr^{2+}	$3d^4$	325–440	1.25	0.07	0.07	0.11
Mn^{2+}	$3d^5$	249–420	1.18	0	0	0
Fe^{2+}	$3d^6$	274–442	1.26	0.08	0.03	0.03
Co^{2+}	$3d^7$	328–441	1.39	0.21	0.27	0.17
Ni^{2+}	$3d^8$	393–441	1.88	0.69	0.88	0.72
Zn^{2+}	$3d^{10}$	352–441	1.01	≤ 0.18	0	0