Point defects and long-range order

A. F. Andreev
P. L. Kapitsa Institute of Physical Problems, Russian Academy of Sciences, 117334 Moscow, Russia

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Point defects in three-dimensional systems exhibit a unique topological characteristic which is associated with the slowness of the decrease of a perturbation of the order parameter and which changes the character of the ordering. The plasticity of crystals which is due to point defects should exist as a thermodynamically equilibrium phenomenon. Fluctuations of the concentration of point defects destroy the equilibrium faceting of crystals. © *1995 American Institute of Physics.*

At low concentration point defects do not destroy long-range order in three-dimensional systems (see Ref. 1, §14) because perturbations of the order parameter decay quite rapidly with increasing distance from a defect. As the typical simple examples, we shall consider the effect of 1) vortex rings and other quasiparticles on the long-range order of superfluid ^{4}He and 2) point defects of a lattice, specifically, dislocation loops, on the long-range order in crystals. In both cases the perturbation of the order parameter (phase of the wave function of the condensate in ^{4}He and the displacement vector in a crystal) at large distances is of a dipole character, i.e., it decreases inversely as the squared distance from a point defect. The key result of the present work is the conclusion that, although such a decrease is rapid enough so as not to destroy the long-range order, it is still so slow that it changes substantially the character of the ordering. The slowness of the decay of a perturbation gives rise to the existence of a unique topological characteristic, which is common to all point defects of a dipole type and which is determined by the asymptotic behavior of the perturbation at large distances. In the case of ^{4}He the change in the character of the ordering consists of the appearance of a rotational (normal) part of the average velocity of the liquid. It is interesting to note that electric and magnetic dipoles in macroscopic electrodynamics also exhibit such a topological characteristic, and in the approach developed here the rotational character of the velocity of the normal component of a superfluid liquid has the same topological origin as the rotational character of the electric and magnetic inductions which is due to the nonuniform distribution of dipole moments.

The case of a superfluid liquid is an illustration of the general approach which is being developed, although in our case it does not lead to new observable results. In contrast, for crystals the result of our study is a general assertion about the plasticity resulting from point defects. The old argument about whether or not point defects could be responsible for plasticity, understood as the possibility of a change in the macroscopic shape of the crystal without a change in the shape of the unit cell, initially ended with a general negative answer.[2] In Ref. 3, it was noted that since dislocation loops with a macroscopic radius are, in any case, a source of plasticity, "elementary carriers" of plasticity, i.e., point defects of minimum energy which have a nonzero dislocation moment, should be present in any crystal. The result of the present work is the assertion that any point defect, specifically, a vacancy, has a dislocation moment. This moment is actually calculated below. For this reason it can be asserted that the experimentally observed[4] plasticity of noncubic crystals, in contradistinction of the opinion stated in Ref. 5, should exist as a thermodynamically equilibrium phenomenon. Plasticity coexists with the crystalline long-range order essentially in the same manner as the rotational motion of the normal component coexists in a superfluid liquid with the long-range order with respect to the phase of the condensate. It is important to underscore that thermally activated point defects exist in any crystal at finite temperature. Point defects are more likely to be elementary excitations than defects. A change in the character of the long-range order as a result of such elementary excitations, as we shall show below and as was noted previously in Ref. 6, is important for resolving the question of the possibility of equilibrium faceting of crystals. This question has become urgent in the last few years in connection with the appearance of studies by, on the one hand, Balibar's group,[7] to which claims have confirmed experimentally the model theory of Nozieres,[8] which is incompatible with plasticity, and, on the other, Babkin *et al.*,[9] which has indicated that faceting in the generally accepted sense does not exist.

1. We consider superfluid ^{4}He with vortex rings or other point defects. The only property of a point defect which is important for us is that the velocity of a defect is small compared to the velocity of sound. This makes it possible to regard the liquid as incompressible. The phase φ of the wave function of the condensate satisfies Laplace's equation $\Delta\varphi=0$, the asymptotic behavior of whose solution at distances $|\mathbf{r}|$ much greater than the size of the defect has the form

$$\varphi(\mathbf{r})=\frac{1}{2}\,\mathbf{s}\nabla\left(\frac{1}{r}\right)=-\frac{(\mathbf{sr})}{2r^3}, \tag{1}$$

where $\mathbf{s}$ is a constant vector characterizing the defect. For a vortex ring with a macroscopic radius we have $\mathbf{s}=\pi R^2\mathbf{n}$, where R is the radius of the ring, and $\mathbf{n}$ is the unit orientation vector.

Let the defects be distributed, on the average, uniformly with density n in the liquid. To simplify the formulas, we shall assume that the parameter $\mathbf{s}$ has the same value for all defects (in general, summation over the type of defects must be performed in the formulas). We shall consider the change $\delta\varphi$ in the phase along a rectilinear contour of macroscopic length δl, assumed, for definiteness, to be parallel to the z axis, and we shall average over the coordinates of the defects. We use a method based on the concept of an effective cross section of a process, well-known from the classical theory of the scattering of particles. This method makes it possible to reduce the averaging over the coordinates of the scattering centers in the problem of one scattered particle to the problem of averaging over impact parameters of the scattered particles relative to one scattering center. Following this method, we consider the change in the order parameter (1) along contours which are parallel to the z axis. The distribution of the contours over the values of the "impact parameters" $\vec{\rho}$ is uniform, i.e., the probability dw of having a contour in an element of area $d^2\rho$ is equal to $Nd^2\rho$. Here $\vec{\rho}$ is the two-dimensional radius vector, $\mathbf{r}=(\vec{\rho},z)$, $\vec{\rho}=(x,y)$, the defect is located at the origin of the coordinates, and the two-dimensional density N of the contours is related to the spatial density of defects in the initial problem by the relation $n\,\delta l = N$. We consider the average value of the phase (1) for fixed z:

$$\langle \varphi(z) \rangle \equiv \int \varphi(\vec{\rho},z)\,dw = N \int \varphi(\vec{\rho},z)\,d^2\rho = -\pi \frac{z}{|z|} s_z N. \tag{2}$$

The latter formula is valid for any z satisfying the following two conditions: 1) $|z|$ is large compared to a defect, which is necessary in order to use the asymptotic relation (1), and 2) $|z| \ll n^{-1/3}$, which makes it possible to disregard the perturbation of the phase by other defects.

The average phase as a function of z near a defect thus has a very characteristic singularity of the type $z/|z|$. This is the topological property of dipole point defects which we discussed at the beginning of this paper. At distances $|z| \ll n^{-1/3}$ the phase undergoes a "topological" jump

$$\langle \delta\varphi \rangle = -2\pi s_z N = -2\pi s_z n\,\delta l, \tag{3}$$

which is not accompanied by singularities of the gradient $\nabla\varphi$.

We introduce the effective cross section σ_z of the process in which the phase changes as $\varphi \to \varphi + 1$ along a rectilinear contour running parallel to the z axis. We define this change by the formula $\langle \delta\varphi \rangle = N\sigma_z$. We have $\sigma_z = -2\pi s_z$. We call attention to the fact that for a vortex ring such an effective cross section corresponds precisely to a topological jump in phase $\varphi \to \varphi - 2\pi$ on a "cut" along the surface of the ring with area s_z; this cut is necessary in order to guarantee that the phase is single-valued in the space external with respect to the ring. Equation (3) has a more general character. It relates the topological jump for any point defect to its universal asymptotic characteristic $\mathbf{s}$ without providing any information about the properties of the solution in the region of the order of the dimensions of the defect.

Equation (3) determines the "topological" part $\langle \delta\varphi \rangle / \delta l$ of the average gradient of the phase. The existence of this part means that the operations of averaging and differentiation with respect to z do not commute. We have $(\partial/\partial z)\langle \varphi \rangle = \langle \partial\varphi/\partial z \rangle - 2\pi s_z n$ or, because of the latitude (arbitrariness) in the choice of the direction of the z axis, we have $\nabla\langle \varphi \rangle = \langle \nabla\varphi \rangle - 2\pi \mathbf{s} n$. The latter formula acquires a standard form, if we introduce the potential velocity $\mathbf{v}_s = (\hbar/m)\nabla\langle \varphi \rangle$ of the superfluid component and the average velocity $\mathbf{v} = (\hbar/m)\langle \nabla\varphi \rangle$, which in our case differs from the average mass flux $\mathbf{j}$ by the constant factor $1/\rho$, where ρ is the density of the liquid. We obtain

$$\mathbf{v} = \mathbf{v}_s + (1/\rho)\mathbf{p} n, \tag{4}$$

where $\mathbf{p} = (2\pi\hbar/m)\rho\mathbf{s}$ is the well-known[10] value of the momentum of a quasiparticle. The long-range order with respect to the phase $\langle \varphi \rangle$ in the presence of defects is characterized by the vortex character of the macroscopic velocity $\mathbf{v}$ and by the existence of a normal component.

We note that the analog of Eq. (4) in macroscopic electrodynamics are the formulas

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{d} n, \quad \mathbf{B} = \mathbf{H} + 4\pi\mathbf{m} n,$$

where **d** and **m** are the electric and magnetic moments of the dipoles, and n is the density of the dipoles. These formulas can be easily derived on the basis of the approach developed here by examining the topological jumps of the scalar potential of the electric or magnetic fields (the potential fields after averaging are **E** and **H**) or examining (for the magnetic field) the topological jumps of the vector potential.

2. The analog of Eq. (4) for a crystal containing dislocation loops with macroscopic radius is the relation (see Ref. 11, § 29)

$$w_{ik}=W_{ik}-d_{ik}n, \qquad (5)$$

where w_{ik} and W_{ik} are tensors of, respectively, the elastic and total distortions, $d_{ik}=s_i b_k$ is the dislocation moment of a loop, **s** is the vector of the geometric area of the loop, **b** is Burgers vector, and n is the number of loops per unit volume. The tensor W_{ik} is the analog of $\mathbf{v}_s$, since it is the gradient of the vector **u** of a geometric displacement of the medium: $W_{ik}=\nabla_i u_k$. The tensor w_{ik} determines the exact periods $\mathbf{a}_\alpha=\mathbf{a}_\alpha^{(0)}+\delta\mathbf{a}_\alpha$, $\alpha=1$, 2, and 3, of the lattice of the crystal in the state of thermodynamic equilibrium, which corresponds to a uniform distribution of defects over the volume: $\delta a_{\alpha i}=w_{ki}a_{\alpha k}^{(0)}$. Here $\mathbf{a}_\alpha^{(0)}$ are the periods in the undeformed state in the absence of defects. For a crystal with a low concentration of point defects the periods $\mathbf{A}_\alpha=\mathbf{a}_\alpha^{(0)}+\delta\mathbf{A}_\alpha$, where $\delta A_{\alpha i}=W_{ki}a_{\alpha k}^{(0)}$, also have a direct physical meaning.[3] These are the lattice periods in the space between the defects and far from each of them. The methods of x-ray crystallographic analysis, in principle, permit determining (see Ref. 1, § 26) both sets of periods. The plastic distortion is equal to the change $\delta(d_{ik}n)$ in the density of the dislocation moment during the deformation process. Since a rotation of the crystal as a whole is not accompanied by a redistribution of defects and plastic deformation, it is actually necessary to know the symmetric part $p_{ik}=1/2(d_{ik}+d_{ki})$ of the dislocation moment. Equation (5), which is symmetrized with respect to the indices i and k, will be derived below and p_{ik} will thereby be calculated for any point defects.

The analog of Eq. (1) for a crystal is the asymptotic form of the elastic displacement $\mathbf{u}(\mathbf{r})$ at large distances from a defect (see Ref. 2):

$$\mathbf{u}_i(\mathbf{r})=E_{kl}\nabla_k G_{il}(\mathbf{r}), \qquad (6)$$

where $G_{ik}(\mathbf{r})$ is the Green's tensor for the equations of equilibrium of the crystal, $E_{ik}=\partial E/\partial u_{ik}$ is a symmetric tensor, and $E=E(u_{ik})$ is the deformation-dependent energy of the defect. The analog of Eq. (2) is the relation

$$\langle u_i(z)\rangle=N\int u_i(\vec{\rho},z)d^2\rho=iNE_{zk}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\,k_z e^{ik_z z}G_{ik}(0,0,k_z),$$

where $G_{ik}(\mathbf{k})$ are the Fourier components of the Green's tensor, which satisfy the equation $\lambda_{imnl}k_m k_n G_{lk}(\mathbf{k})=\delta_{ik}$, where λ_{iklm} is the tensor of elastic moduli. A simple integration gives

$$\langle u_i(z)\rangle=-\frac{1}{2}\frac{z}{|z|}Ng_{ik}E_{zk},$$

where g_{ik} is a matrix which is the reciprocal of the matrix λ_{izzk}.

The topological jump $\langle\delta u_i\rangle$ of the displacement is given by the formula

$$\lambda_{izzk}\langle \delta u_k\rangle = -E_{iz} n\,\delta l.$$

By virtue of the latitude in choosing the direction of the z axis, we thus obtain

$$\lambda_{ilmk}\{\nabla_m\langle u_k\rangle - \langle \nabla_m u_k\rangle\} = -E_{il} n.$$

Setting

$$w_{ik} = \langle \nabla_i u_k\rangle, \quad W_{ik} = \nabla_i\langle u_k\rangle,$$

we find

$$u_{ik} = U_{ik} - p_{ik} n, \tag{7}$$

where u_{ik} and U_{ik} are the symmetric parts of w_{ik} and W_{ik}, respectively. The symmetrized tensor p_{ik} of the dislocation moment of a point defect is determined by the universal formula $E_{ik} = -\lambda_{iklm} p_{lm}$. The fact that the deformation dependence of the energy of a dislocation loop of macroscopic radius is determined by this formula is well known (see Ref. 11, § 28). Our assertion is that any defect whose energy depends naturally on the deformation has a nonzero p_{ik} determined by this formula.

The ordering of a crystal with point defects, specifically, thermally activated defects, whose concentration is proportional to $\exp(-E/T)$, is characterized by the presence of two sets of periods $\mathbf{a}_\alpha$ and $\mathbf{A}_\alpha$ (analogous to the two velocities $\mathbf{v}$ and $\mathbf{v}_s$ in a superfluid liquid). The periods $\mathbf{A}_\alpha$ are not real periods of the average density of the particles. In weakly nonuniform states of the crystal, however, the change in these periods in space is determined by the distortion tensor W_{ik}, which is the gradient $\nabla_i u_k$ of the displacement vector $\mathbf{u}$. The correlation function of the fluctuations $\Delta\mathbf{u}$ of the displacements

$$\langle [\Delta u_i(\mathbf{L}) - \Delta u_i(0)][\Delta u_k(\mathbf{L}) - \Delta u_k(0)]\rangle = K_{ik}(\mathbf{L})$$

is finite in the limit $|\mathbf{L}| \to \infty$. This is the criterion for crystalline long-range order.

The values of the real periods $\mathbf{a}_\alpha$ of the average density in weakly nonuniform states are determined by the distortion tensor w_{ik}, which is not a gradient of any displacement vector. This accounts for the plasticity of the crystal, which is analogous to the vortex character of the velocity $\mathbf{v} = \mathbf{j}/\rho$ of an incompressible superfluid liquid.

In model Hamiltonians describing the properties of the surface of a crystal[8] a periodic lattice potential, which should have real lattice periods $\mathbf{a}_\alpha$, is introduced. The physical reality of such a potential can be substantiated if the correlation function of the fluctuations Δw_{ik} of the distortions

$$Q_{ik}(\mathbf{L}) = \left\langle \left(\int_0^{\mathbf{L}} \Delta w_{li}\, dx_l \right)\left(\int_0^{\mathbf{L}} \Delta w_{mk}\, dx_m \right)\right\rangle,$$

is finite in the limit $|\mathbf{L}| \to \infty$. Here the integrals extend along the straight lines connecting $\mathbf{r} = \mathbf{L}$ and $\mathbf{r} = 0$. However, the fluctuations Δn in the concentration of point defects destroy this periodic potential. Disregarding the noncritical fluctuations ΔW_{ik}, we have

$$Q_{ik}(\mathbf{L})=\left\langle \int_0^{\mathbf{L}} \Delta u_{il} dx_l \int_0^{\mathbf{L}} \Delta u_{km} dx_m \right\rangle$$

$$=p_{il}p_{km}\frac{L_l L_m}{L^2}\int_0^L dz \int_0^L dz' \langle \Delta n(0,z)\Delta n(0,z')\rangle = p_{il}p_{km}\frac{L_l L_m}{L^2} L \frac{\bar{n}}{a^2},$$

where $\bar{n}$ is the average density of the critical defects, and a is of the order of the interatomic distance. For thermally activated defects, we have $Q_{ik}(L) \propto Le^{-E/T}$. This mechanism of destruction of the "periodic lattice potential" was proposed previously in Ref. 6, but the critical defects were complex defects with unknown E. It can now be asserted that point defects with the minimum energy (vacancies for ^4He crystals) are critical. The thermodynamically equilibrium faceting of crystals cannot exist at finite temperatures, and phase transitions accompanying the appearance of the kinetic "non-equilibrium" faceting are related to the vanishing of the coefficient of growth of the crystal on the singular faces.

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[1] M. A. Krivoglaz, *Theory of X-Ray and Thermal-Neutron Scattering by Real Crystals* [in Russian], Nauka, Moscow, 1967.
[2] J. D. Eshelby in *Solid State Physics*, Academic Press, New York, 1956, Vol. 3, p. 113, Izdatel'stvo Inostr. Lit., Moscow, 1963, p. 57.
[3] A. F. Andreev, Ya. B. Bazaliy, and A. D. Savischev, J. Low Temp. Phys. **88**, 101 (1992).
[4] R. Feder and A. S. Nowick, Phys. Rev. B **5**, 1244 (1972).
[5] R. Feder and A. S. Nowick, Phys. Rev. B **5**, 1238 (1972).
[6] A. F. Andreev, JETP Lett. **52**, 619 (1990).
[7] E. Rolley, E. Chevalier, C. Guthmann, and S. Balibar, Phys. Rev. Lett. **72**, 872 (1994); J. Low Temp. Phys. **99**, 851 (1995).
[8] P. Nozieses in *Solids Far from Equilibrium*, edited by C. Godreche, Cambridge University Press, 1991.
[9] A. V. Babkin, H. Alles, P. J. Hakonen *et al.*, J. Low Temp. Phys. (in press)
[10] E. M. Lifshitz and L. P. Pitaevskiĭ, *Statistical Physics*, Pergamon Press, N. Y. [Russian edition, Nauka, Moscow, 1978, Part 2, Problem 1 for §29].
[11] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, Pergamon Press, N. Y. [Russian edition, Nauka, Moscow, 1965].

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