TRANSITION ENTROPY OF DEFECT MELTING

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Received 12 January 1983
Revised manuscript received 1 March 1983

We use the newly developed gauge theory of line-like defects to calculate, in the mean field approximation, the entropy for the combined proliferation of dislocations and disclinations. The result is $\Delta S \approx 2.4$ per site, in good agreement with the melting entropy in most materials.

Thirty years ago, Shockley [1] and somewhat later Feynman [2] suggested that melting and the superfluid normal transition ^{4}He could be understood as a proliferation of dislocation and vortex lines, respectively. If both are right, it is hard to understand why one transition is of first, the other of second order. Until recently, theoretical formulations had two unsatisfactory choices: Either they left out the elastic long-range forces between the defect lines [3]. Then the transition was second order. Or they included them in an approximate way by calculating the "black body" energy of their fluctuations. This led to a cubic term in the disorder parameter and thus to a first-order transition [4], in analogy with similar calculations for the superconductive phase transition [5]. Since both systems, vortices as well as dislocations, have similar long-range forces it remained unclear why in ^{4}He the long-range forces were apparently irrelevant to the order of the transition while in melting they were essential. A possible solution to this puzzle came in sight when the author showed that defect lines with low core energies proliferate in a first-order transition [6,7]. This is due to the existence of a tricritical point in the Ginzburg–Landau theory of superconductivity when the ratio of penetration and coherence length K equals [8] $\approx 0.8/\sqrt{2}$ [‡1]. In terms of the parameters of the Ginzburg–Landau theory, the electric charge e and the quartic coupling g of the complex order field $\psi(x)$, K is given by $-(g/2e^2)^{1/2}$. But dislocation lines follow the same type of theory [6], except with magnetic and order fields replaced by elastic and disorder fields, respectively. They are characterized by a K value in which g measures the short-range steric repulsion between lines and $e^2 = \mu a^3/T$ is given by shear modulus μ, temperature T, and lattice constant a [6,7]. Thus lines with a small steric repulsion, or equivalently, with a low core energy, do undergo a first-order transition. This result was confirmed in two dimensions by independent Monte Carlo calculations [10].

It is the purpose of this paper to point out that manipulations of the core energies are not necessary. There exists a simple and powerful mechanism which drives the melting transition first order. It is the proliferation of defect lines of the rotational type, called disclinations, which always accompanies the proliferation of dislocation lines. Let us recall that, according to Volterra, dislocation lines are translational defects which can be constructed by removing a semi-infinite slice of thickness $\boldsymbol{b}$ from the material and joining the open faces. Disclinations, on the other hand, arise from a similar removal of a wedge-like section of opening angle $\boldsymbol{\Omega}$. ($\boldsymbol{b}$ and $\boldsymbol{\Omega}$ are called Burgers and Frank vectors, respectively.)

[‡1] In the superfluid ^{4}He, the K parameter is $\approx 1.2/\sqrt{2}$ as shown recently by the author in ref. [9].

It is obvious that disclinations carry an enormous stress energy. At first sight, this seems to preclude them from thermal generation. We shall demonstrate, however, that this is an illusion. Quite on the contrary, disclinations play a crucial role in driving the melting transition. The reason lies in the fact that dislocation lines can screen the long-range elastic forces between disclinations such that both line systems can proliferate simultaneously. It is the coupling between the two systems which is responsible for the first order of the melting transition.

The starting point is the lattice representation of the partition function of stresses and defects as given in ref. [7] ‡2:

$$Z \propto \prod_{x,i,j} \int_{-\infty}^{\infty} \mathrm{d}h_{ij}(x)\, \delta(\bar\nabla_i h_{ij}) \sum_{\bar\alpha_{ij}, \bar\theta_{ij}} \delta_{\bar\nabla_j \bar\theta_{ij},0}\, \delta_{\bar\nabla_j \bar\alpha_{ij}, \tilde\theta_i}$$

$$\times \exp\left[-\tau \sum_x \left(\sigma_{ij}(x)^2 - \frac{\nu}{1+\nu}\sigma_{ii}(x)^2\right) + 2\pi \mathrm{i} \sum_x h_{ij}(x)\, \eta_{ij}(x)\right], \tag{1}$$

where ν is the Poisson number, τ the reduced temperature (expressed in terms of physical temperature T and elastic Lame constant μ as $\tau \equiv T\pi^2/\mu a^3$, σ_{ij} a reduced version of the symmetric divergenceless stress tensor written in the double-curl form $\sigma_{ij} \equiv \epsilon_{ikl}\epsilon_{jmn}\bar\nabla_k \bar\nabla_m h_{ln}(x - l - n)$ and $\bar\eta_{ij} = \bar\theta_{ij} - \frac{1}{2}\bar\nabla_m(\epsilon_{mjl}\bar\alpha_{li} + (i \to j) + \epsilon_{ijl}\bar\alpha_{lm})$ is the defect density with $\bar\alpha_{li}$, $\bar\theta_{ij}$ being the dislocation and disclination density, respectively [7] ‡3 ($\tilde\theta_i \equiv \epsilon_{ijk}\bar\theta_{jk}$). All three defect fields are integer valued. The divergence conditions in the summations guarantee that disclinations form closed lines, dislocation lines can end only on disclination lines, and that the defect density $\eta_{ij}(x)$ is symmetric and divergenceless, $\bar\nabla_i \eta_{ij}(x) = 0$. Let us recall that in the absence of disclinations, the h_{ij} integrals can simply be executed with the result

$$Z \propto \sum_{\bar\alpha_{ij}} \delta_{\bar\nabla_j \bar\alpha_{ij},0} \exp\left[-\frac{\pi^2}{\tau}\sum_k \left(|\bar\alpha^{(2,2)}(k)|^2 + |\bar\alpha^{(2,-2)}(k)|^2 + \frac{1+\nu}{1-\nu}|\bar\alpha^{(1,0)}(k)|^2\right)\left(6 - 2\sum_i \cos k_i\right)^{-1}\right], \tag{2}$$

where the superscripts (s, λ) denote the lattice analogues of the spin s helicity λ projections [6,7]. This is a system of closed dislocation lines with $1/r$ forces.

In the presence of disclinations, progress can be made by enforcing the integer constraint on $\bar\alpha_{ij}$ by means of a set of angular integrations such that we can write the purely dislocational part of Z as

$$Z^{\alpha}_{\tilde\theta} \propto \sum_{\bar\alpha_{ij}} \delta_{\bar\nabla_j \bar\alpha_{ij}, \tilde\theta_i} \exp\left(2\pi \mathrm{i} \sum_x h_{ij}\epsilon_{ikl}\bar\nabla_k \bar\alpha_{lj}\right)$$

$$\propto \lim_{t\to 0} \prod_x \int_{-\pi}^{\pi} \frac{\mathrm{d}\omega_i(x)}{2\pi} \exp\left(\frac{1}{t}\sum_{x,i,j}[\cos(\nabla_j\omega_i - 2\pi\epsilon_{ikl}\nabla_k h_{lj}) - 1] + \mathrm{i}\sum_x \omega_i \tilde\theta_i\right). \tag{3}$$

This is verified by applying Villain's approximation (which for $t \to 0$ is exact),

$$Z^{\alpha}_{\tilde\theta} \propto \lim_{t\to 0} \prod_{x,i} \int_{-\pi}^{\pi} \frac{\mathrm{d}\omega_i(x)}{2\pi} \sum_{m_{ij}} \exp\left(-\frac{1}{2t}\sum_x (\nabla_j\omega_i - 2\pi\epsilon_{ikl}\nabla_k h_{lj} - 2\pi m_{ij})^2 + \mathrm{i}\omega_i\tilde\theta_i\right), \tag{4}$$

and introducing α_{ij} as an auxiliary integration variable

‡2 We work on a simple cubic crystal, for simplicity, and use the symbols $\nabla_i\phi(x) = \phi(x + i) - \phi(x)$, $\bar\nabla_i\phi(x) = \phi(x) - \phi(x - i)$ to denote lattice derivatives. Stress is treated in the continuum approximation, i.e., we neglect the third elastic constant.

‡3 For further discussion of this splitting see refs. [8,11].

$$Z_{\theta}^{\alpha} \propto \lim_{t\to 0} \prod_{x,i,j} \int_{-\infty}^{\infty} \mathrm{d}\alpha_{ij}(x) \prod_{x,i} \int_{-\pi}^{\pi} \frac{\mathrm{d}\omega_i(x)}{2\pi}$$

$$\times \exp\Big(\sum_x [-\tfrac{1}{2} t\alpha_{ij}^2 + \mathrm{i}\alpha_{ij}(\nabla_j\omega_i - 2\pi\epsilon_{ikl}\nabla_h h_{lj} - 2\pi m_{ij})^2 + \mathrm{i}\omega_i\widetilde{\theta}_i]\Big)\,, \tag{5}$$

whereupon the sum over m_{ij} squeezes α_{ij} to integers $\overline{\alpha}_{ij} = 0, \pm 1, ...$ while the integration over ω_i enforces the correct divergence condition $\overline{\nabla}_i\alpha_{ij} = \widetilde{\theta}_i$. Let us now turn Z_{θ}^{α} into a dislocation field theory using the method of refs. [8,9,11,12]. This gives, with $\psi_i \equiv \psi_i^{\mathrm{R}} + \mathrm{i}\psi_i^{\mathrm{I}}$,

$$Z_{\theta}^{\alpha} \propto \prod_{x,i} \int_{-\infty}^{\infty} \mathrm{d}\psi_i^{\mathrm{R}} \int_{-\infty}^{\infty} \mathrm{d}\psi_i^{\mathrm{I}}(x) \exp\Big(\sum_{x,i} \log I_{\widetilde{\theta}_i}(|\widetilde{\psi}_i|) + \log\cos[|\psi_i|\arg(\widetilde{\psi}_i^{\mathrm{I}}/\widetilde{\psi}_i^{\mathrm{R}})]\Big)\,, \tag{6}$$

where $\widetilde{\psi} \equiv (1 + D_i\overline{D}_i/2D)^{1/2}\psi$, with

$$D_j\psi_i(x) = \psi_i(x+j)\exp[-2\pi\mathrm{i}\epsilon_{ikl}\nabla_k h_{lj}(x)] - \psi_i(x),$$

$$\overline{D}_j\psi_i(x) = \psi_i(x) - \psi_i(x-j)\exp[2\pi\mathrm{i}\epsilon_{ikl}\nabla_k h_{lj}(x-j)],$$

being covariant versions of the lattice derivatives, and $I_{\widetilde{\theta}}$ are the Bessel functions of integer order.

In the absence of disclinations, the transition would be second order. From the discussion in refs. [8,9] we know that this remains true after fluctuation correction. Therefore, the energy (6) can be expanded à la Landau as

$$E \sim \sum_{x,i} (\tfrac{1}{24} \Sigma_j |D_j\psi_i|^2 - \tfrac{1}{4}|\psi_i|^2 + \tfrac{1}{64}|\psi_i|^4 + ...). \tag{7}$$

For simplicity, let us use the long-wavelength approximation $D_j\psi_i \sim (\nabla_j - 2\pi\mathrm{i}\epsilon_{jkl}\nabla_k h_{lj})\psi_i$ and consider the effective potential for constant $\psi_j \equiv \psi$. Then we see [6,7] that the phonon field h_{lj} acquires a "mass" $M^2 \equiv (\pi^2/6\tau)|\psi|^2$, since (7) contains a term

$$\tfrac{4}{24}\pi^2|\psi|^2 \sum_x \epsilon_{ikl}\nabla_k h_{lj}\epsilon_{ik'l'}\nabla_{k'}h_{l'j} = \tau M^2 \sum_k h_{lj}(k)(P^{(2,2)} + P^{(2,-2)} + P^{\mathrm{L}})_{lj,l'j'}h_{l'j'}(k)K^2. \tag{8}$$

Here $K^2 \equiv 6 - 2\Sigma_{i=1}^3 \cos k_i$ denotes the Fourier transform of $-\overline{\nabla}_i\nabla_i$. Including (8) in the stress energy, phonon loops produce the following elastic self-energy for dislocation lines [7]

$$(1/12\tau)\pi^2 v(\mathbf{0})[1 + \tfrac{2}{3}\nu/(1-\nu)]\sum_j |\psi_j|^2, \tag{9}$$

where $v(0) = \Sigma_K 1/K^2 = 0.253$ is the lattice Coulomb potential at the origin. At sufficiently small temperature, this prohibits dislocations. For $\tau > \tau_c^{\nu}$, however, the dislocation field destabilizes and undergoes a phase transition, as discussed in ref. [7]. If interpreted as melting, this mean field transition would have a too high melting temperature, i.e. a too low Lindmann parameter $L \sim 100$. Close to τ_c^{ν}, the effective potential has the Landau approximation

$$V(|\psi|) \sim \tfrac{1}{4}(\tau_c^{\nu}/\tau - 1) \sum_j |\psi_j|^2 + \tfrac{1}{64}\sum_j |\psi_j|^4. \tag{10}$$

Let us now include disclinations. Integrating out the phonon field produces an interaction

$$\exp\Big(-\frac{\pi^2}{\tau}\sum_k \{(|\theta^{(2,2)}(k)|^2 + |\theta^{(2,2)}(k)|^2)/(K^4 + M^2K^2) + |\theta^{(2)}(k)|^2/\{[(1-\nu)/(1+\nu)]K^4 + M^2K^2\}^{-1}\}\Big) . \tag{11}$$

The correlation functions can be split as $M^{-2}[(K^{-2} - (K^2 + M^2)^{-1}])$ and $M^{-2}\{K^{-2} - \{K^2 + [(1+\nu)/(1-\nu)]M^2\}^{-1}\}$. We can now easily discuss the changes produced by the disclinations in the effective potential of dislocations. For simplicity, let us for a moment restrict the sum over θ_{ij} to symmetric tensors only. Then $\widetilde{\theta}_i = 0$ and the additional potential to (9) is simply

$$\Delta V(|\psi|) = -\log Z^{\mathrm{disclin}}$$

$$= -\log \sum_{\theta_{ij}} \delta_{\nabla_j\theta_{ij},0} \exp\Big\{-\frac{\pi^2}{\tau M^2}\sum_k \Big[(|\theta^{(2,2)}(k)|^2 + |\theta^{(2,-2)}(k)|^2)\Big(\frac{1}{K^2} - \frac{1}{K^2 + M^2}\Big)$$

$$+ |\theta^{\mathrm{L}}(k)|^2\Big(\frac{1}{K^2} - \frac{1}{K^2 + [(1+\nu)/(1-\nu)]M^2}\Big)\Big]\Big\} . \tag{12}$$

For small M^2, the disclination potentials diverge logarithmically such that no disclinations are possible. For larger M^2, we can neglect the massive second parts of the correlation functions and remain with a system in which the disclination loops have the same properties as the previous dislocation system with the replacement $\tau \to \tau M^2$ and $\tau_c^\nu \to \tau_c^0$. Thus they have an effective potential on their own of the form

$$V^{\mathrm{disclin}}(|\phi_i|) = \tfrac{1}{4}(\tau_c^0/\tau M^2 - 1)\sum_i |\phi_i|^2 + \tfrac{1}{64}\sum_i |\phi_i|^4 + ..., \tag{13}$$

where ϕ_i are now fields describing disclinations. The additional potential $\Delta V(|\psi|)$ is obtained by minimizing this expression at fixed $M^2 = (\pi^2/6\tau)|\psi|^2$. There is a second-order phase transition at $\tau M^2 > \tau_c^0$ and $V(|\psi|)$ behaves close to this region as

$$\Delta V(|\psi|) \sim 0, \qquad |\psi|^2 < 2v(0),$$

$$\sim -\sum_i [2v(0)/|\psi|^2 - 1]^2, \quad |\psi|^2 > 2v(0). \tag{14}$$

The total dislocation potential $(V + \Delta V)(|\psi|)$ is shown in fig. 1 [‡4]. There is a first-order melting transition at

‡4 This is the *full* potential involving all powers of ψ in (7) and (13). It turns out that the transition lies in the Landau regime of the dislocation energy (7) (i.e., the lowest terms (10) are appropriate), but somewhat outside of the disclination's Landau regime [i.e., approximation (14) requires corrections from higher powers in (13)]. It is amusing to find out that the full transition entropy ΔS happens to be the same as in a Landau approximation (13) and (14).

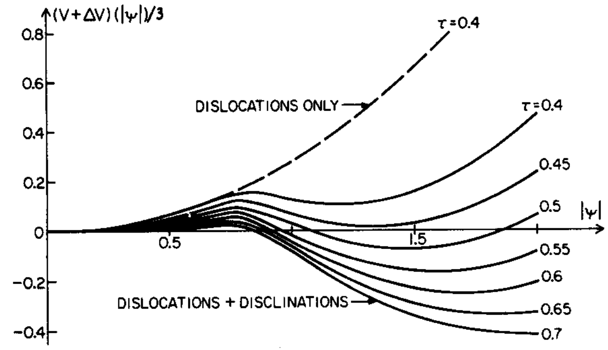

Fig. 1. The effective potential for dislocations in the presence of disclinations. At $\tau \sim 0.4$ there is a first-order phase transition due to the depression caused by disclinations.

$\tau_{melt} \sim 0.4$, corresponding to a Lindemann parameter $L \sim 140$. The entropy jump is $\Delta S \sim 2.4$ per site in units of the Boltzmann constant. Both numbers agree with experiment for many materials [13] [‡5].

The physical mechanism creating the entropy jump can be described as follows: A virtual increase in the disorder parameter $|\psi|$ has the effect of changing, the in partition function of disclination lines, the contribution of pairs of parallel line elements from $\exp(\tau^{-1}R)$ to $\exp[-(6/\pi^2|\psi|^2)R^{-1}]$. In this way they come to behave the same way as previously the dislocation lines with an effective temperature $\frac{1}{6}\pi^2|\psi|^2$. If the physical temperature τ is held fixed, an increase in $|\psi|^2$ is perceived just like a heating process such that there exists a critical $|\psi_c| \sim 0.7$ beyond which the disclinations proliferate. This produces a depression of the effective potential, i.e. it becomes easier to produce more dislocations because of the disclinations. By looking at this process for lower and lower physical temperature, there will be a value $\tau_{melt} \sim 0.456$ where the point of depression has the same energy as $|\psi| = 0$. At this temperature, the disorder parameter $|\psi|$ can jump from zero to the new value $|\psi| \sim 1.4$ without cost in energy and the crystal melts in a first-order phase transition. For $\tau \sim 0.5$ the minimim is $(V + \Delta V)_{min} \sim -0.23$. From this we calculate $\Delta S \sim -\tau\partial(V + \Delta V)_{min}/\partial\tau \sim 2.4$ per site.

This value is twice as large as what is found in most materials. The discrepancy has a simple explanation: In the present calculation we have treated dislocations and disclinations as completely independent defects. In an actual crystal, this is not true. Dislocations can be viewed as bound states of two neighboring disclinations with opposite Frank vector. Conversely, disclinations can arise from sheets of dislocations. Thus only one type of defect fields should be enough to explain the melting process, provided we can handle the bound state problem. Since this problem is very difficult we have taken the approximation of treating the fundamental and the bound state defects both at the same level. This approximation is familiar from low-energy nucleon scattering where the deuteron may be treated as an elementary particle. Such an approximation breaks down in processes where the constituents become separated. But this is precisely what happens here. From the point of view of a more proper pure disclination model, the present calculation shows that in the melting process the bound states, the dislocations, proliferate, and that this screens the forces holding the constituent disclinations together. From this point of view, melting is really a *disclination deconfining* transition. It is this combination of proliferation and splitting which makes the transition first order. Obviously, such a more proper treatment would wind up with only half as much disorder in the molten state than the present calculation and this explains our excessive transition entropy.

Let us now see that inclusion of the antisymmetric parts of θ_{ij} cannot change this picture essentially. For this we note that $\log I_{\tilde{\theta}_i}(|\psi_i|)$ differs from $\log I_0(|\psi_i|)$ mostly by a term $|\tilde{\theta}_i| \log|\psi_i| - \log(2^n n!)$. The remainder depends very little on $\tilde{\theta}_i$ if this runs through low integers. But this means that the contribution of $\tilde{\theta}_i$ to the partition function can be taken into account approximately by another exponential

$$\exp(\Sigma_{x,i}\{|\tilde{\theta}_i|\log|\psi_i| + \log\cos[|\tilde{\theta}_i|\mathrm{arctg}(\tilde{\psi}_i^{\mathrm{I}}/\tilde{\psi}_i^{\mathrm{R}})]\})$$

in (12). This is just a core energy to the antisymmetric part of θ_{ij} which, moreover, is not coupled elastically. For small $|\psi|^2$, $\tilde{\theta}_i$ cannot be excited at all and the sum (12) becomes a pure sum over the symmetric tensors θ_{ij}. For large $|\psi|^2$, the antisymmetric parts can also proliferate, thus producing a further depression of $(V + \Delta V)(|\psi|)$ above some critical value $|\psi_{c_2}|^2$, which will at most increase the transition heat.

A word is necessary concerning the quality of the mean field approximation used in our calculations. Since the transition is found to be *strongly* first order, we expect extremely small fluctuation corrections. Thus it is quite improbable that the first order obtained at the mean field level could be wiped out by fluctuation corrections, as it happened in the extremely weak first-order case of ref. [5].

It should be pointed out that all our discussion was limited to pure linear elasticity which is not entirely consistent since core energies of the defects appear only in those components which are coupled. In actual systems, the nonlinear effects are expected to produce core energies also in the uncoupled components $\theta^{(s,\lambda)}(k)$. These are, in fact, necessary to make the sums (2) and (12) convergent. We have omitted such extra core energies only to keep the formulas simple and make it easier to concentrate on the essential mechanism which leads to the first-order

[‡5] See also ref. [14] for a discussion of present beliefs about transition heats.

transition. In some pyhsical systems, it seems possible that nonlinear effects are very powerful leading to a qualitatively different relation between the core energies of disclinations and dislocation. In that case it might happen that disclinations are so strongly suppressed that the proliferation of the two types of defects occurs successively. This scenario seems to take place in the transition sequence smectic A→nematic→isotropic, in liquid crystals [15]. The reason for this may lie in the rod shape of the molecules.

Let us finally note that in two dimensions, the backfeeding effect of disclinations is of similar importance and deserves a separate discussion [16].

The author thanks Drs. A. Ami and S. Alexander for discussions. This research was supported in part by the National Science Foundation, grant no. PHY77-27084.

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