

## Kinetics of the Superconducting Transition

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We study the time evolution of a superconductor, following a quench from the normal state, in two dimensions. For a type-I superconductor, quenched into a region where the normal state is metastable, the normal-superconductor phase boundary exhibits a dynamical instability similar to, but not identical with, that observed in solidification. In the case of a quench into the Meissner phase of a type-II superconductor, the average vortex spacing  $d$  as a function of time  $t$  is found to exhibit a crossover from  $d \sim t^{1/2}$  to  $d \sim \ln t$ , the crossover time being an increasing function of the Ginzburg-Landau parameter  $\kappa$ .

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The superconducting transition in metals occurs very slowly, with equilibration times of as much as 30 min reported in laboratory experiments.<sup>1</sup> Mendelssohn and Pontius<sup>1</sup> were apparently the first to give a physical explanation of this phenomenon, by pointing out that the superconducting transition is accompanied by eddy currents which dampen the motion of the propagating phase boundary between normal and superconducting regions, and a quantitative theory was given by Pippard<sup>2</sup> and Lifshitz.<sup>3</sup> Subsequent experiments by Faber<sup>4,5</sup> are in semiquantitative agreement with theoretical predictions for the rate of phase propagation. This body of early work was conducted on what are now called type-I superconductors.

More recently, interest in the kinetics of phase transitions *per se* has focused on the phenomenon of dynamic scaling;<sup>6</sup> both experiment<sup>7</sup> and computer simulation<sup>8</sup> for the approach to equilibrium of, e.g., a binary alloy during spinodal decomposition observe the development of a spatial pattern characterized by a single time-dependent length scale  $l$ . It is found that  $l$  varies in time  $t$  as  $l \sim t^\phi$ , with  $\phi$  consistent with a value of  $\frac{1}{3}$ . Theoretical<sup>9</sup> and computational<sup>10,11</sup> studies on systems with a continuous symmetry suggest that dynamical scaling occurs there too, albeit with a different value for the scaling exponent  $\phi$ , although the possibility of multiscaling has not been firmly excluded.

In this paper, we present preliminary results on the kinetics of the superconducting transition, for both type-I and type-II superconductors. Our results apply to two-dimensional superconductors with two-dimensional electromagnetism. Qualitative aspects of our results are expected to be valid in three dimensions. In type-I superconductors, the kinetics may proceed through two alternative bulk mechanisms, analogous to nucleation and spinodal decomposition, depending upon whether the external field  $H_e$  is respectively above or below  $H_{c2}$ .<sup>12</sup> We demonstrate a similarity to the dynamics of a crystal growing into its undercooled melt, and accordingly a linear stability analysis predicts a dynamical instability

of a planar normal-superconducting ( $N$ - $S$ ) boundary, as observed by Faber but attributed to surface effects.<sup>4,5</sup> This well-known instability<sup>13</sup> is responsible for the ubiquitous dendritic patterns encountered in solidification.<sup>14</sup> The similarity is not complete, however, and there are differences due to the presence of two length scales associated with the  $N$ - $S$  boundary—the correlation length  $\xi$  and the electromagnetic penetration depth  $\lambda$ .

We have studied the “spinodal” regime using two-dimensional numerical simulations of the quench into the Meissner phase of a type-II superconductor at zero external field, and have monitored the time evolution of the average intervortex separation  $d(t)$  during vortex-antivortex annihilation. In the case of a neutral superfluid, our earlier work<sup>11</sup> indicated that  $d \sim t^{1/2}$ . This can be interpreted as arising from overdamped vortex motion in the intervortex potential as a function of separation  $r$ ,  $U(r) \sim \ln r$ . In the case of the charged superfluid considered here, the intervortex potential is logarithmic for  $r \ll \lambda$ , but decays exponentially for  $r \gg \lambda$ . Thus, we might anticipate that at short times the dynamics is similar to that of the neutral superfluid, but at longer times, when  $r \sim \lambda$ , there should be a crossover to  $d \sim \ln t$ . This is indeed what we observe.

*Equations of motion.*— We begin by writing down the time-dependent Ginzburg-Landau (TDGL) equations that govern the dynamics of the superconducting order parameter  $\psi(\mathbf{r}, t)$  and the electromagnetic vector potential  $\mathbf{A}(\mathbf{r}, t)$ :

$$\gamma \frac{\partial \psi}{\partial t} = - \left[ a + b |\psi|^2 + \frac{1}{4m} \left( i \hbar \nabla + \frac{2e}{c} \mathbf{A} \right)^2 \right] \psi \quad (1)$$

and

$$\frac{4\pi\sigma}{c^2} \frac{\partial \mathbf{A}}{\partial t} = - \nabla \times (\nabla \times \mathbf{A}) - \frac{2\pi e}{mc} \left[ \psi^* \left( i \hbar \nabla + \frac{2e}{c} \mathbf{A} \right) \psi + \text{c.c.} \right], \quad (2)$$

where  $e$  and  $m$  are the charge and mass, respectively, of

the electron,  $c$  is the speed of light in vacuum,  $\sigma$  is the normal-state conductivity, and  $\gamma$ ,  $a$ , and  $b$  are phenomenological constants, which can be estimated using the BCS theory if desired.<sup>15</sup> By assuming local charge neutrality<sup>16</sup> and using a gauge in which the scalar potential is zero, the above equations must be supplemented by the constraint  $\nabla \cdot \mathbf{A} = 0$ .<sup>17</sup>

*Linear stability of sharp N-S interface on type-I superconductors.*—Qualitative features of the dynamics may be obtained by assuming the existence of a sharp interface on the scale of  $\lambda$  between the normal and superconducting states, with the interface characteristics on the scale of  $\xi$  subsumed into the surface tension. The validity of this assumption is discussed further below. Consider a N-S interface moving in two dimensions into the normal state with velocity  $v_n$  along its normal  $\mathbf{n}$ , in an external magnetic field  $H_e < H_c$ . Taking the curl of Eq. (2), we find that

$$\frac{\partial \mathbf{B}}{\partial t} = D \nabla^2 \mathbf{B} \quad (3)$$

in the normal state, where  $D = c^2/4\pi\sigma$  and zero penetration of the magnetic field into the superconducting state is assumed. Using the Maxwell equations at a moving interface,  $(v_n/c)\mathbf{B} = \mathbf{n} \times \mathbf{E}$ , and taking  $\mathbf{B}$  perpendicular to the plane of the system, we obtain

$$v_n B_{ns} = -D(\nabla \mathbf{B}) \cdot \mathbf{n}, \quad (4)$$

where  $B_{ns}$  is the magnetic field on the N-S boundary. In early work<sup>2-4</sup>  $B_{ns}$  was assumed to be the thermodynamic critical field. However, this is only true for a planar interface in thermodynamic equilibrium, and must be modified for a curved N-S interface. Local mechanical equilibrium near the interface requires the minimization of total free energy at fixed temperature and total volume:  $\delta F = -P_s \delta V^s - P_n \delta V^n + \delta \int \sigma_{ns}(\mathbf{n}) dS = 0$ , where  $F$ ,  $P$ , and  $V$  denote free energy, pressure, and volume, the subscripts  $n$ ,  $s$ , and  $ns$  indicate contributions from normal phase, superconducting phase, and N-S phase boundaries, respectively, and  $\sigma_{ns}$  is the surface energy of the N-S interface. In two dimensions, the variational calculation yields  $\Delta P \equiv P_s - P_n = [\sigma_{ns}(\theta) + \sigma''_{ns}(\theta)]\mathcal{K}$ , where  $\theta$

is the angle between  $\mathbf{n}$  and the reference direction in space, and  $\mathcal{K}$  is the curvature of the interface. A more complicated form of this relation exists in three dimensions. Equating the chemical potential of the two phases we obtain the shift in field at coexistence due to the curved interface:  $\Delta H \equiv B_{ns} - H_c = -4\pi\Delta P/H$ , which gives  $\Delta H = -(4\pi/H_c)(\sigma_{ns} + \sigma''_{ns})\mathcal{K}$ . The modified ‘‘Gibbs-Thomson’’ boundary condition is then<sup>18</sup>

$$B_{ns} = H_c \left[ 1 - \frac{4\pi}{H_c^2} (\sigma_{ns} + \sigma''_{ns}) \mathcal{K} \right] = H_c [1 - d_0 \mathcal{K}], \quad (5)$$

where we have defined a capillary length  $d_0(\theta) = (\sigma_{ns} + \sigma''_{ns})/(H_c^2/4\pi)$ . For isotropic, extreme type-I superconductors, with a correlation length of  $\xi$ , it can be shown<sup>19</sup> that  $d_0 = 2\sqrt{2}\xi/3$ .

The analogy between Eqs. (3), (4), and (5) and the one-side model of dendritic solidification<sup>20</sup> implies that a planar N-S interface, advancing at a speed  $v$ , will become linearly unstable<sup>13</sup> on length scales greater than a critical length  $L_c \approx 2\pi(d_0 D/v)^{1/2}$ . A superconducting core growing into a supercooled normal state will generate complex interface structures, as seen in our numerical simulations. The instability only occurs in the plane perpendicular to the external field direction: There is no new linear instability arising from the vector character of the magnetic field. The reverse process of flux penetration into a superconducting state, in a transverse field  $H_e > H_c$ , is perfectly stable, and has been studied by Faber and others.

The above analogy is incomplete because the assumption of a sharp interface is not valid. Unstable vortex structures on a scale of order  $\xi$  can be generated in time-dependent processes. In type-II superconductors, these destroy the sharp interface, and even in weakly type-I superconductors, this instability is present, and observed in the ‘‘spinodal’’ regime of type-I superconductors in both the time-dependent simulations of Frahm, Ullah, and Dorsey<sup>21</sup> (and discussed there in terms of phase slippage) and in our own simulations.

*Time-dependent simulations.*—After scaling  $r' = r/\xi$ ,  $H' = H/\sqrt{2}H_c$ ,  $A' = A/\sqrt{2}H_c\lambda$ ,  $t' = t/(4\pi\sigma\xi^2/c^2)$ , and dropping primes, we rewrite Eq. (1) as

$$\Gamma \frac{\partial \psi}{\partial t} = \psi(1 - |\psi|^2) + \exp \left[ i \int \mathbf{A} \cdot d\mathbf{r} \right] \nabla^2 \left[ \psi \exp \left[ -i \int \mathbf{A} \cdot d\mathbf{r} \right] \right], \quad (6)$$

$$\frac{\partial \mathbf{A}}{\partial t} = \nabla^2 \mathbf{A} + \frac{1}{\kappa^2} \text{Im} \left\{ \psi^* \exp \left[ i \int \mathbf{A} \cdot d\mathbf{r} \right] \nabla \left[ \psi \exp \left[ -i \int \mathbf{A} \cdot d\mathbf{r} \right] \right] \right\}, \quad (7)$$

where  $\Gamma = \gamma/(4\pi\sigma\xi^2 a/c^2)$  can be estimated using the BCS theory<sup>22</sup> to be  $\Gamma = [3\pi^2 mc^2/28\zeta(3)\hbar](k_B T_c/E_F)(1/\sigma)$ , and  $\kappa \equiv \lambda/\xi$ . Taking  $\sigma = 1 \mu\Omega^{-1} \text{cm}^{-1}$ ,  $T_c/E_F \sim 10^{-3}$ , we find that  $\Gamma \sim 0.8$ . Therefore we choose  $\Gamma = 1$  as a representative value.

We have used an explicit finite-difference scheme to solve these equations on a two-dimensional square lattice, with the order parameter defined on the nodes and the vector potential on the links.<sup>23</sup> The magnetic field is restricted to be perpendicular to the plane of the superconductor. The system is surrounded by an insulator held in constant external magnetic field  $H_e$ . The boundary conditions on the sides of our sample are  $\partial\psi/\partial\mathbf{n} = 0$  and  $\mathbf{A} \cdot \mathbf{n} = 0$  which guarantee

that no current flows out of the sample. The constraint  $\nabla \cdot \mathbf{A} = 0$  is imposed at each time step. Full details of our simulations will be published elsewhere.

*Phase propagation in a type-I superconductor.*— We have studied the dynamics of a stable normal phase invading the superconducting phase, and the dynamics of a superconducting phase growing into both the metastable and unstable normal phase. A typical time sequence of the unstable growth process, starting from random initial conditions for the order parameter and  $H = H_c$ , is shown in Fig. 1. The similarity with spinodal decomposition is apparent. In the case of a quench into the metastable state, we find that seeds larger than the critical nucleus do grow unstably, as the stability analysis suggests.

*Type-II superconductor at zero field.*— We have performed simulations of the zero-field transition in type-II superconductors, with a cell dynamic scheme (CDS) used previously to study the approach to equilibrium of a system with a complex order parameter (but no gauge field).<sup>11</sup> The CDS algorithm updated the order-parameter field equation (6), and we used an explicit algorithm for the London equation (7). Periodic boundary conditions enabled us to study the process of vortex annihilation. The CDS algorithm coarse grains the system at the scale of  $\xi$ , and so is suitable only for the type-II case. The control parameter in these simulations,  $G$ , may be related to  $\kappa$  by measuring the correlation length in the simulation: We find  $G \approx 1/2\kappa$ .

We have monitored the average intervortex spacing as

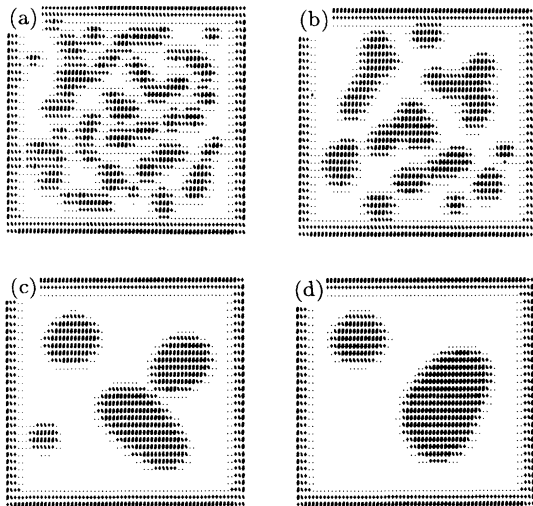


FIG. 1. Time sequence of the growth of the Meissner phase in a type-I superconductor, at zero temperature, with the field quenched below the spinodal line  $H_{c2}$ . The grey scale is a measure of field strength, with white indicating field-free regions. The parameters are a lattice size of  $60 \times 60$ ,  $H_c = 0.2$ ,  $\kappa = 0.4$ . Space and time discretization units are  $dt = 0.03$  and  $dx = 0.7$ . (a)  $t = 800$ . (b)  $t = 2800$ . (c)  $t = 69600$ . (d)  $t = 175600$ .

a function of time and  $G$  for a lattice of size  $256 \times 256$ , averaged over 30 initial conditions, and our results are shown in Fig. 2. For  $G = 0.02$  we find that  $d \sim t^\phi$ , with an exponent close to  $\phi = 0.375$ . This is the same exponent found in the neutral case ( $G = 0$ ) in the same time range<sup>11</sup> and we expect that for this or lower values of  $G$  we will recover  $\phi \sim 0.5$  at longer times.

For  $G$  in the range of 0.2–0.4, our simulations show clear departures from power-law behavior, with  $d \sim \ln t$ , as shown in Fig. 2. Even this slow dynamics may not be the true asymptotic behavior, at least in two dimensions: At very long times, the combination of the weak interaction between vortices separated by distances large compared to  $\lambda$  and possible weak pinning effects from the lattice can cause a freezing of the dynamics. Future work will determine whether or not there is dynamical scaling during the superconductor transition, as well as examining the physically relevant cases of three-dimensional electromagnetism with both two- and three-dimensional superconductivity.

Our results question the identification of patterns in the intermediate state of type-I superconductors as true equilibrium structures. Furthermore, there is the interesting possibility that the domain structures exhibit dynamical scaling in the same way that has been predicted for the domain structures in block copolymer melts.<sup>24</sup>

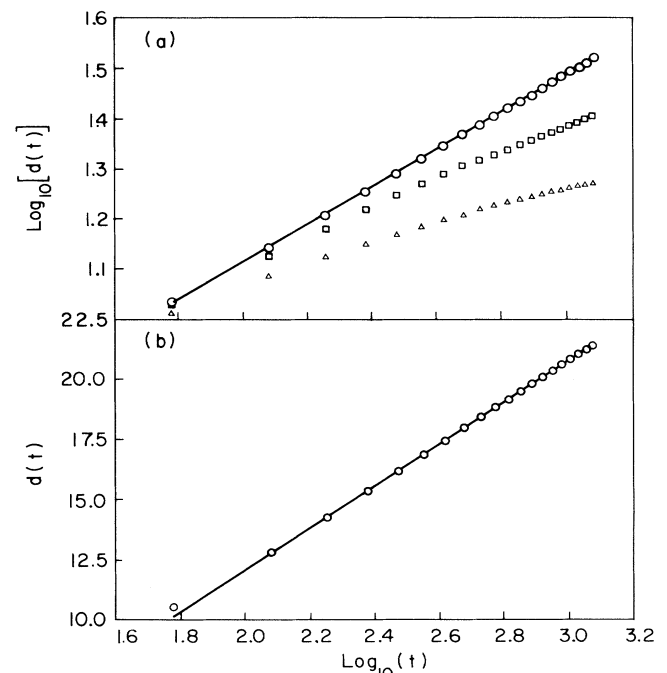


FIG. 2. Intervortex spacing  $d$  for various values of  $G$  with  $H_c = 0$  on a lattice of size  $256 \times 256$ . (a)  $\log_{10} d$  vs  $\log_{10} t$ , averaged over 30 initial conditions, for  $G = 0.02$  (circles), 0.2 (squares), and 0.4 (triangles). For  $G = 0.02$ , the solid line is a fit by  $d \approx t^\phi$ , with  $\phi \sim 0.38$ . (b)  $d$  vs  $\log_{10} t$  for  $G = 0.3$ , averaged over 60 initial conditions.

We conclude by mentioning another possible implication of our results. Vortexlike defects in grand unified theories are candidates for the seeds of galaxies in the evolving Universe.<sup>25</sup> In this scenario, the correlations between vortices would be relevant to the observed correlations of galaxies. Our results show that these correlations may be sensitive to whether the vortices are defects in a theory with local gauge symmetry (superconductor case) or with only global gauge symmetry (neutral superfluid case).

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<sup>1</sup>W. H. Keesom and P. H. van Laer, *Physica (Utrecht)* **3**, 173 (1936); **4**, 499 (1937); **5**, 986 (1938); K. Mendelssohn and R. B. Pontius, *Physica (Utrecht)* **3**, 327 (1936); J. G. Daunt, *Philos. Mag.* **24**, 361 (1937); H. Grayson Smith and K. C. Mann, *Phys. Rev.* **54**, 766 (1938); N. E. Alexeyevsky, *J. Phys. USSR* **9**, 217 (1945); J. Babiskin, *Phys. Rev.* **85**, 104 (1952).

<sup>2</sup>A. B. Pippard, *Philos. Mag.* **41**, 243 (1950).

<sup>3</sup>I. M. Lifshitz, *Zh. Eksp. Teor. Fiz.* **20**, 834 (1950).

<sup>4</sup>T. E. Faber, *Proc. Roy. Soc. London A* **214**, 392 (1952); **219**, 75 (1953); **223**, 174 (1954).

<sup>5</sup>T. E. Faber and A. B. Pippard, *Prog. Low Temp. Phys.* **1**, 159 (1955).

<sup>6</sup>For reviews, see H. Furukawa, *Adv. Phys.* **34**, 703 (1985); J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8.

<sup>7</sup>B. D. Gaulin, S. Spooner, and Y. Morii, *Phys. Rev. Lett.* **59**, 668 (1987).

<sup>8</sup>A. Shinozaki and Y. Oono, *Phys. Rev. Lett.* **66**, 173 (1991).

<sup>9</sup>G. F. Mazenko and M. Zannetti, *Phys. Rev. B* **32**, 4565 (1985); F. de Pasquale and P. Tartaglia, *Phys. Rev. B* **33**, 2081 (1986); H. Toyoki and K. Honda, *Prog. Theor. Phys.* **78**, 273 (1987); A. Coniglio and M. Zannetti, *Europhys. Lett.* **10**, 575 (1989); A. J. Bray, *Phys. Rev. Lett.* **62**, 2841 (1989).

<sup>10</sup>H. Toyoki, in *Dynamics of Ordering Processes in Condensed Matter*, edited by S. Komura and H. Furukawa (Plenum, New York, 1988); H. Nishimori and T. Nukii, *J. Phys. Soc. Jpn.* **58**, 563 (1989); T. J. Newman, A. J. Bray, and M. A. Moore, *Phys. Rev. B* **42**, 4514 (1990).

<sup>11</sup>M. Mondello and N. Goldenfeld, *Phys. Rev. A* **42**, 5865 (1990).

<sup>12</sup>See, for example, M. Tinkham, *Introduction to Superconductivity* (Krieger, Malabar, 1985), p. 129.

<sup>13</sup>W. W. Mullins and R. F. Sekerka, *J. Appl. Phys.* **34**, 323 (1963).

<sup>14</sup>See, for example, F. Liu and N. Goldenfeld, *Phys. Rev. A* **42**, 895 (1990), and references therein.

<sup>15</sup>We have neglected time derivatives higher than first in Maxwell's equations and latent-heat effects.

<sup>16</sup>N. R. Werthamer, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969).

<sup>17</sup>Although the TDGL equations are strictly valid only for gapless type-II superconductors very close to the superconducting transition temperature  $T_c$ , we shall assume here that they give a qualitative and even semiquantitative description of the phase-transition kinetics. See Ref. 12, p. 273, and Ref. 16.

<sup>18</sup>Taking into account the anisotropic surface energy corresponds to an effective inverse mass tensor in the TDGL equations. The Gibbs-Thomson boundary condition for the isotropic case may be found in C. G. Kuper, *Philos. Mag.* **42**, 961 (1951).

<sup>19</sup>P. G. de Gennes, *Superconductivity of Metals and Alloys* (Addison-Wesley, Redwood City, 1989), p. 180.

<sup>20</sup>J. S. Langer, *Rev. Mod. Phys.* **52**, 1 (1980).

<sup>21</sup>H. Frahm, S. Ullah, and A. T. Dorsey, preceding Letter, *Phys. Rev. Lett.* **66**, 3067 (1991).

<sup>22</sup>A. A. Abrikosov, *Fundamentals of the Theory of Metals* (Elsevier, New York, 1988).

<sup>23</sup>Y. Enomoto and R. Kato, *J. Phys. Condens. Matter* **3**, 375 (1991), have performed simulations of the TDGL equations using a different method from the one used here.

<sup>24</sup>F. Liu and N. Goldenfeld, *Phys. Rev. A* **39**, 4805 (1989); M. Bahiana and Y. Oono, *Phys. Rev. A* **41**, 6763 (1990).

<sup>25</sup>T. W. B. Kibble, *J. Phys. A* **9**, 1387 (1976); I. Chuang, R. Durrer, N. Turok, and B. Yurke, *Science* (to be published).