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Supercooling across first-order phase transitions in vortex matter

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Abstract. Hysteresis in cycling through first-order phase transitions in vortex matter, akin to the well-studied phenomenon of supercooling of water, has been discussed in literature. Hysteresis can be seen while varying either temperature T or magnetic field H (and thus the density of vortices). Our recent work on phase transitions with two control variables shows that the observable region of metastability of the supercooled phase would depend on the path followed in $H-T$ space, and will be larger when T is lowered at constant H compared to the case when H is lowered at constant T. We discuss the effect of isothermal field variations on metastable supercooled states produced by field-cooling. This path dependence is not *a priori* applicable to metastability caused by reduced diffusivity or hindered kinetics.

Keywords. Supercooling; metastability; superconductors; vortex matter; first-order transition.

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In recent years first-order phase transitions in vortex matter have been studied with both temperature and magnetic field (or vortex density) as the control variable, and the question of metastability has been addressed [1–3]. The phase transition temperature $T_{\rm C}(H)$ [4] drops as magnetic field is raised, as depicted in figure 1. Vortex matter contracts on being heated from the ordered (solid) phase to the disordered (liquid) phase, similar to the behaviour of ice at pressures below 200 MPa [5]. Hysteresis has been reported, with both field and temperature as the control variable, across the vortex–lattice melting transition [1,2]. We have also reported supercooling of the higher entropy vortex–solid phase in the polycrystalline samples of C15 Laves phase superconductor $CeRu_2$, both on reducing field and on reducing temperature, and have found that the supercooled state persists farther in the latter case [3,6]. Similar signatures of supercooling have been reported in single crystals of $CeRu_2$, $NbSe_2$ and $YBa_2Cu_3O_7$ [7–9].

The standard treatment [10] of supercooling across a first-order transition considers that only temperature is varied and other possible control variables (like magnetic field) are held constant. The free-energy density is expressed in terms of the order parameter S as

$$f(T,S) = (r/2)S^2 - wS^3 + uS^4, \qquad (1)$$

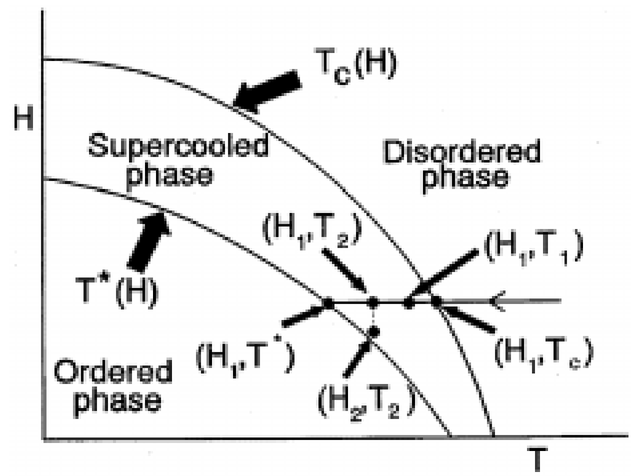

Figure 1. We show a schematic of the phase transition line $T_{\rm C}(H)$ and the stability limit $T^*(H)$ for the supercooled state: (H_1, T_1) and (H_1, T_2) indicate supercooled states when vortex matter is cooled in a field H_1. See text for details.

where w and u are positive and temperature-independent [10]. (We will assume in this paper that symmetry does not prohibit terms of odd order. If it does, then the free energy would be expressed as $f = (r/2)S^2 - wS^4 + uS^6$, and it is easy to follow and carry through all arguments in this paper. The assumption of the form of eq. (1) is thus made without loss of generality.) At $T = T_{\rm C}$ the two stable states with $f = 0$, are at $S = 0$ and at $S = S_{\rm C} = w/(2u)$. These are separated by an energy barrier peaking at $S = S_{\rm B} = w/(4u)$, of height $f_{\rm B} = w^4/(256u^3)$. These results are independent of any assumption about the detailed temperature dependence of $r(T)$. The standard treatment [10] assumes that $r(T) = a[T - T^*]$, where a is positive and temperature independent, and where $\mathrm{d}^2 f/\mathrm{d}S^2$ at $S = 0$ vanishes at $T = T^*$. Simple algebra shows that the limit of metastability on cooling is reached at $T^* = T_{\rm C} - w^2/(2ua)$. The limit of metastability on heating is reached when the ordered state no longer has a local minimum in $f(S)$. This occurs at $T^{**} = T_{\rm C} + w^2/(16ua)$. As noted above, supercooling (or superheating) can persist till T^* (or T^{**}) only in the limit of infinitesimal fluctuations. The barrier height around $S = 0$ drops continuously as T is lowered below $T_{\rm C}$, and this is depicted in figure 2. In the presence of a fluctuation of energy $e_{\rm f}$, supercooling will terminate at T_0 where the energy barrier satisfies

$$f_{\rm B}(T_0) \approx [e_{\rm f} + k_{\rm B}T_0]. \tag{2}$$

Similarly, the barrier height around the ordered state drops continuously to zero as T is raised towards T^{**}, and this is depicted in figure 3. The fluctuation energy in the ordered state will dictate when superheating will terminate.

The formulation stated above is of course valid for a first order transition in vortex-matter as a function of T.

Vortex-matter phase transitions are encountered in H–T space and the limit of supercooling (T^*) is now a function of H. This standard treatment has recently been extended to the case where one has two control variables, viz. density and temperature. It has

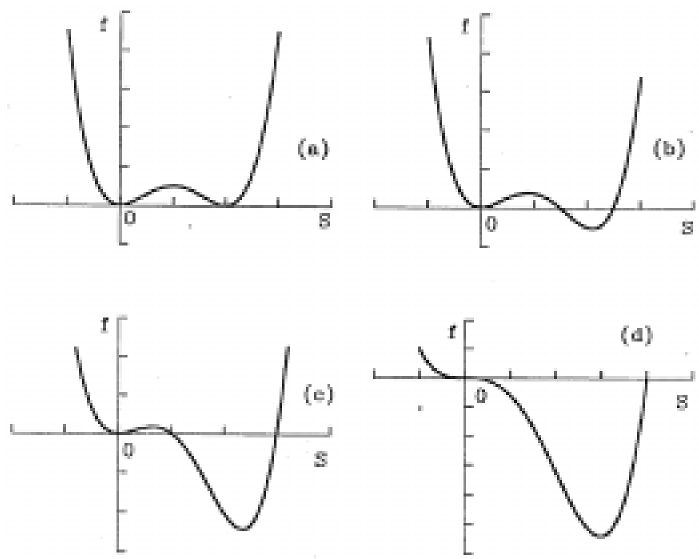

Figure 2. We show schematic free energy curves for (**a**) $T = T_{\mathrm{C}}$, (**b**) $T = T_1 < T_{\mathrm{C}}$, (**c**) $T = T_2 < T_1$ and (**d**) $T = T^*$. The disordered state sits in a local minimum and is stable against infinitesimal fluctuations for $T_{\mathrm{C}} > T > T^*$. This local minimum becomes shallower as T is lowered below T_{C} and the disordered state at T_2 is unstable to a smaller fluctuation energy than at T_1.

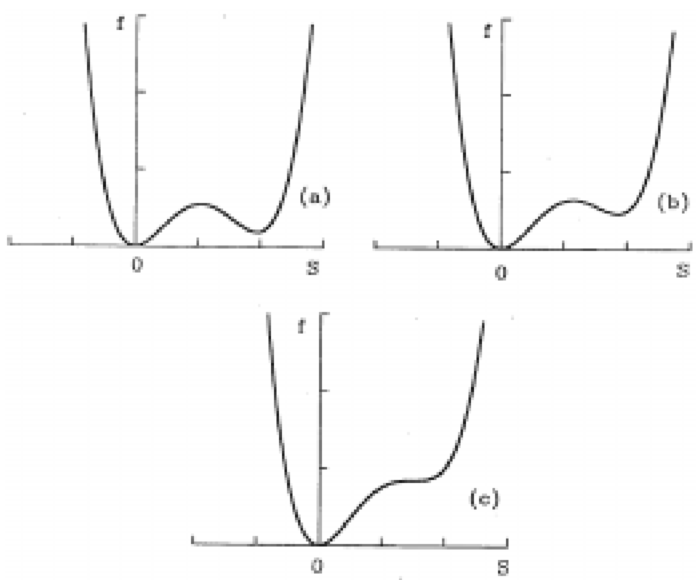

Figure 3. We show schematic free energy curves for (**a**) $T = T_3 > T_{\mathrm{C}}$, (**b**) $T = T_4 > T_3$ and (**c**) $T = T^{**}$. The ordered state sits in a local minimum and is stable against infinitesimal fluctuations for $T_{\mathrm{C}} < T < T^{**}$.

been shown [11] that when $T_{\rm C}$ falls with rising density (as in water–ice below 200 MPa), then $T_{\rm C}-T^*$ will rise with rising density. If, on the other hand, $T_{\rm C}$ rises with rising density (as in water–ice above 200 MPa), then $T_{\rm C}-T^*$ will fall with rising density. This appears consistent with experiments on ice (see figure 5 of [5]). The density of vortices rises with increasing H, and these predictions are also consistent with our data on single crystal $CeRu_2$ [12]. The first order phase boundary $T_{\rm C}(H)$ can be crossed by following arbitrary paths in H–T space.

It has been argued, however, that the very procedure of varying H introduces fluctuations, and these fluctuations will terminate supercooling at a line $T_0(H)$ which lies above the $T^*(H)$ line [11]. (The disordered phase can be supercooled close to $T^*(H)$ only if T is lowered in constant H, i.e., in the field-cooled mode). While ref. [11] used a simple polynomial form of f, the qualitative conclusion that the $T_0(H)$ line lies above the $T^*(H)$ line does not change if one chooses a more complicated form of f. We now wish to consider the case where the sample is cooled in constant H to a temperature T satisfying $T^*(H) < T < T_0(H)$, and then subjected to an isothermal field variation. The isothermal field variation ΔH produces a fluctuation energy $e_{\rm f}$ which increases monotonically (but nonlinearly) with ΔH [11]. The field-cooled state at T corresponds to supercooling of the disordered phase, and it sits in a local minimum of free-energy as depicted in figure 2(b) and (c). The fluctuation energy $e_{\rm f}$ (and thus the isothermal field variations, ΔH) required to cross-over to the absolute minimum in free energy (the ordered state) will be smaller when the free energy barrier $f_{\rm B}$ defining the local minimum is smaller. By definition, $f_{\rm B}$ vanishes on the $T^*(H)$ line. We further note that $f_{\rm B}$ decreases monotonically as one approaches the $T^*(H)$ line by monotonically varying one control variable. Since one can move from (H_1,T_1) to (H_1,T_2) to $(H_1,T^*(H_1))$ by continuously decreasing T (see figure 1), $f_{\rm B}$ will be smaller at (H_1,T_2) than at (H_1,T_1). Similarly, one can field-cool to (H_1,T_2) and to (H_2,T_2) with H_2 smaller than H_1. Since one can go from (H_1,T_2) to (H_2,T_2) to the $T^*(H)$ line at T_2 by monotonically reducing H it follows immediately that the free energy barrier $f_{\rm B}$ separating the disordered metastable state from the globally stable ordered state will be smaller at (H_2,T_2) than at (H_1,T_2). The fluctuation energy $e_{\rm f}$, and thus the isothermal field variation, ΔH, required to cause the metastable state to transform to the ordered state will be smaller at H_2 than at H_1. Our heuristic arguments can similarly be used for various other experimentally accessible paths in (H,T) space.

We have argued that an extension [11] of the standard theory of supercooling can explain various path-dependent history effects seen in first-order phase transitions in vortex matter. We now argue that metastability and hysteresis can have two distinct origins, with their characteristic path-dependences. One is associated with supercooling or superheating across a first order transition, and the supercooled state at (H,T) produced by lowering T in constant H is farther from equilibrium (i.e., it requires a larger perturbation to take the metastable state to the equilibrium state) than the supercooled state produced by lowering H in constant T. Second, hysteresis can also be kinetic in origin, and metastable states would be observed when the volume (say) lags behind the applied pressure because the large viscosity of the molecules does not allow equilibrium to be reached in the experimental time window. This second origin for metastability and hysteresis would be seen *within a glassy phase* (as distinct from across a glass transition) because a glass is defined as a disordered material with viscosity greater than 10^{13} poise. This is also the origin for M–H hysteresis seen in hard superconductors. The hysteresis seen in hard

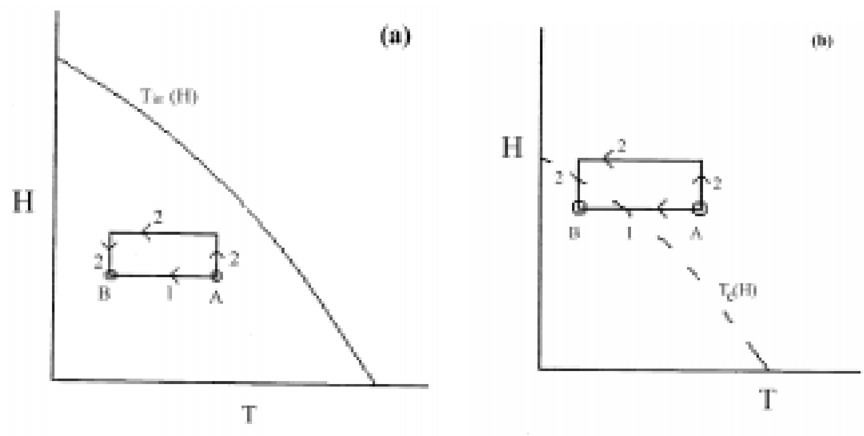

Figure 4. We depict schematically the path-dependence of metastability which is of (**a**) kinetic and (**b**) supercooling origin. In case (a) there is no phase transition separating points A and B. Path 2 produces a state at B which is farther from equilibrium than that produced by path 1. In case (b) points A and B lie on either side of a first order phase transition line $T_C(H)$. Following ref. [11], path 1 produces a state at B that is farther from equilibrium than that produced by path 2.

superconductors as one goes from (H_1, T) to (H_2, T) and back to (H_1, T) is explained within the critical state model as due to pinning, or hindered kinetics, of vortices.

We now discuss the path-dependence of metastability when the origin is due to hindered kinetics. We go from point A to point B by two different paths depicted in figure 4a, with path 1 involving no changes in magnetic field. The critical state model, valid below the irreversibility line of a hard type II superconductor, predicts that path 2 will result in a state which is farther from equilibrium. Note that no phase transition line separates points A and B. In figure 4b we show points A and B lying close to but on opposite sides of a first order phase transition line. The arguments in ref. [11] established that path 1 will result in a state which is farther from equilibrium. In the case of vortex matter, metastabilities due to hindered kinetics alone thus have a path-dependence which is opposite to the metastabilities associated with a first order phase transition. Whether this is applicable to all solids exhibiting hindered kinetics needs to be established.

To conclude, we have considered the path-dependence of metastabilities associated with a first order transition [11] as applicable to vortex matter, and made predictions on the effect of isothermal field variations on metastable states produced by field cooling. We have argued that metastabilities can have two different origins–one kinetic and the other supercooling. Metastabilities that are purely kinetic in origin have a path dependence which is opposite to that of metastabilities associated with a first order transition.

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