Metastabilities in vortex matter

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Abstract

We extend the classical theory for supercooling across first order phase transitions to the case when both density and temperature are control variables. The observable region of metastability then depends on the path followed in this space of two variables. Since the density of vortex matter in superconductors can be easily varied over a wide range by varying applied field, it is ideal for experimental tests. We found, in our studies on the ‘peak effect’ in the mixed state of superconducting CeRu$_2$, supercooled states whose observable region of metastability depends on the path followed in (H,T) space, consistent with our predictions. We also discuss phenomena in hard superconductors that are well understood within Bean’s critical state model. We conclude that the path dependence of metastability associated with hindered kinetics may be opposite to that predicted for metastability associated with supercooling across a first order transition.
INTRODUCTION

The mixed state of type II superconductors is seen for applied fields $H$ lying between the lower ($H_{C1}$) and upper ($H_{C2}$) critical fields. It consists of vortices carrying quantized flux which ideally form a two-dimensional hexagonal lattice under repulsive forces. Can this lattice of vortices undergo structural transitions? Can vortex structures show metastabilities seen in usual condensed matter? These questions assume a broader significance because the density of vortex matter in superconductors can be varied over a wide range (from nearly zero to about $10^{12}$ per cm$^2$) by varying applied magnetic field, and may thus provide better experimental tests for metastabilities around phase transitions.

The period after the discovery of high-$T_C$ superconductors (HTSC) has seen many theoretical works proposing vortex- matter phase transitions [1]. Vortex lattice melting as the field (or temperature) is raised towards the $H_{C2}(T)$ line now stands established as a first order phase transition and experiments have established a latent heat, as well as a jump in equilibrium magnetisation, satisfying the Clausius-Clapeyron relation [2, 3, 4].

Simultaneously, an early theoretical prediction of a first order phase transition in the vortex lattice of paramagnetic superconductors [5, 6, 7], in which the infinitely long vortices get segmented into short strings with a sudden enhancement of pinning [8], (and thus critical current density $J_C$ vs $H$ shows a peak) has been motivating experimentalists into studying in great detail the "peak effect" (PE) in CeRu$_2$. The first thermodynamic signature indicating that the onset of the PE is a first order transition (FOT), consistent with the theoretical prediction of Fulde, Ferrel and Larkin, Ovchinnikov (FFLO), came through the observation that the PE appears at a field $H_u^*$ on increasing field, but vanishes at a lower field $H_d^*$ on decreasing fields [9, 10, 11]. This hysteresis in the occurrence of the PE was taken as the hysteresis expected in a FOT. We have attempted to identify other measurable signals of a FOT. The vortex matter in CeRu$_2$ has been our paradigm, and the FFLO theory has been motivating us, possibly as a red herring. The theory is correct and is still used by theorists in understanding coexisting superconductivity and (weak) magnetism [12]. Since our experiments cannot probe the microscopic nature of the phase in the PE region of CeRu$_2$, we shall not discuss the relevance of FFLO theory to CeRu$_2$ any further in this talk; those interested can see our recent papers [13, 14].

In this talk we shall briefly outline the existing wisdom of experimental tests for a FOT,
and then present our extension to the case where one can interchangeably vary two control parameters to traverse the FOT line. The need for this extension was necessitated by our studies on CeRu$_2$. We shall state new predictions, and discuss experimental verification.

SUPERCOOLING ACROSS FIRST ORDER PHASE TRANSITIONS

A phase transition is defined as an nth-order transition in the Ehrenfest scheme\[15\] if the nth derivatives of the free energy are discontinuous, whereas all lower derivatives are continuous, at the transition point. (The derivatives are taken with respect to the control variables.) The derivative with respect to temperature is entropy and its discontinuity in a FOT implies a latent heat, while the derivative with respect to pressure is volume which should show a discontinuous change at $T_C$. The latent heat and volume change are further related by the Clausius-Clapeyron equation.

The Ehrenfest scheme is ambiguous\[15\] for some phase transitions - one example being the lambda transition in liquid helium. Phase transitions are now classified using an order parameter $S$ that changes across the phase boundary. The change is discontinuous, from $S = 0$ to $S = S_0$ for a FOT, but continuous for a second-order transition. Two phases can coexist at the transition point of a FOT. This is put on a formal footing by writing the free energy as a function of the order parameter $S$. When the control variable (say $T$) corresponds to the transition point ($T_C$), then the free energy $f(S)$ has two equal minima (at $S = 0$ and $S = S_0$) for a FOT\[16\], while there is only one minimum for a second order transition. One can obviously show that a FOT is accompanied by a latent heat and a sudden volume change, consistent with the Ehrenfest scheme.

The existence of two equal minima implies the coexistence of two phases at the transition point; slightly away from the transition point one still has two minima - one global and one local - with slightly unequal values of the free energy $f$. We show in fig. 1a schematic of $f(S)$ curves as the control variable ($T$) is varied from above to below the transition point ($T_C$). The high temperature phase has higher entropy and is ‘disordered’, having an order parameter $S = 0$. while the low temperature phase has a finite (but $T$-dependent) order parameter. Since $S = 0$ continues to correspond to a local minimum in $f(S)$ slightly below $T_C$, one can supercool the higher entropy state below the transition point\[16\]. Similarly one can superheat the ordered phase above the transition point. One thus sees another
experimental characteristic of a FOT, viz. the possibility of hysteresis in the transition point as one varies a control variable. This was the observation\cite{9, 10, 11} that led to the inference that the onset of PE in CeRu$_2$ is a FOT.

Concentrating on supercooling, we note from fig. 1 that the barrier $f_B(T)$ in $f(S)$ separating the metastable state at $S = 0$ from the stable ordered state reduces continuously as $T$ is lowered below $T_C$, and vanishes at the limit of metastability ($T^*$) of the supercooled state\cite{16}. Supercooling is easily observed across the water-ice transition\cite{17}, a FOT familiar to all of us, and we believe that the hysteresis in the onset of PE in CeRu$_2$ is also a manifestation of the same\cite{18, 19}. If the system is in the disordered state at $T < T_C$, then nucleation of the metastable ordered phase occurs, with $f_B(T) > kT$, only by introducing localised fluctuations of large energy $e_f$. The nucleation rate is extremely sensitive to the height of the barrier $f_B$, and carefully purified metastable liquids evolve suddenly from apparent stability to catastrophic growth of the ordered phase\cite{17}. The barrier vanishes below $T^*$, and the unstable disordered state now relaxes into the ordered state by the spontaneous growth of long-wavelength fluctuations of small amplitude, i.e. by spinodal decomposition\cite{17}. (Here we shall assume that the ordered stable phase is formed fast compared to experimental time scales if $f_B(T) \leq [e_f + kT]$, and the system remains in the metastable state if $f_B(T)$ is larger. We shall briefly initiate a discussion on kinetics and kinetic metastabilities in the last section of this paper).

Both the water-ice transition, and the onset of PE in CeRu$_2$, have been studied extensively with density as a second control variable. While the density of water has been varied by varying pressure up to 3 kbar\cite{17}, the density of vortices is varied by varying the applied magnetic field, and the onset of PE in CeRu$_2$ has been tracked from 1 Tesla to 4 Tesla\cite{11}, corresponding to a four-fold change in vortex density. We can now talk of supercooling the disordered $S = 0$ phase, at differing densities, below the $T_C(P)$ corresponding to that density. Can one compare the extent of metastability in such supercooled states? Secondly, we can cross the transition line $T_C(P)$ by varying density rather than by varying temperature. The $f(S)$ curves are defined once a (T,P) point is defined; the $S = 0$ state would be metastable just below the FOT line irrespective of whether the line is crossed by varying $T$ or by varying density. We can thus supercool the disordered phase into the region below the FOT line even by varying density. Can one compare the metastability in a supercooled state, at a point (T,P) below the FOT line, as depending on the path followed to reach this
(T,P) point? Before pursuing this we must emphasize that such questions cropped up in our studies on CeRu$_2$ because it is experimentally easy to follow arbitrary paths in density (magnetic field) and temperature space in the case of vortex matter. The disordered phase here is characterised by a larger critical current density $J_C$ compared to the ordered phase; supercooling is confirmed by measuring the minor hysteresis loops$^{[14, 18, 19]}$ in contrast to the case of supercooled water where one measures diffusivity$^{[17]}$.

We have recently argued that while reduction of temperature at constant density does not a priori cause building up of fluctuations, the very procedure of varying density introduces fluctuations$^{[20]}$. Lowering temperature isothermally can keep $e_f$ zero in ‘carefully purified liquids’. Density variation at constant T, however, builds up $e_f$ even in such systems. It was noted that free energy curves should be plotted for three parameters as $f(P,T,S)$ where $P$ is a generic pressure that implies magnetic field in the case of vortex matter. Supercooling along various paths in (T,P) space involves moving from a $f(P_1,T_1,S)$ curve to $f(P_2,T_2,S)$ curve in this multidimensional space. These curves have two equal minima for (T,P) values lying on the FOT line $T_C(P)$, and the barrier $f_B$ vanishes for (T,P) values lying on a line $T^*(P)$. We refer to this $T^*(P)$ line as the limit of metastability on supercooling. The first point to note is that while $f(P,T,0)$ is weakly dependent on T, it depends strongly on $P$$^{[20]}$. The second point is that the S-dependence of $f(P,T,S)$, for fixed T, is different at different $P$. This originates from the different densities of the ordered and disordered phases, and this was also incorporated by us$^{[20]}$. Finally, we argued that if density is varied then a fraction of the energy change $f(P_1,T,0) - f(P_2,T,0)$ will be randomised into a fluctuation energy $e_f$. This last point$^{[20]}$ looks obvious in the case of vortex matter where vortices get pinned and unpinned as they move, and the energy dissipated in the process is easily measured as the area within the M-H loop. With these physical inputs, we could make the following predictions$^{[20]}$:

1. When $T_C$ falls with rising density as in vortex matter FOT, or in water-ice transition below 2 kbar, then $(T_C - T^*)$ will rise with rising density. If $T_C$ rises with rising density as in water-ice above 2 kbar, and in most other solid-liquid transitions, then $(T_C - T^*)$ will fall with rising density. This prediction is consistent with known data on water$^{[17]}$.

2. The disordered phase can be supercooled up to the limit of metastability $T^*(P)$ only if
T is lowered in constant P. If the $T_C(P)$ line is crossed by lowering P at constant T, then supercooling will terminate at $T_0(P)$ which lies above the $T^*(P)$ line. If $T_C$ falls with rising density, then $(T_0(P) - T^*(P))$ rises with rising density.

3. A supercooled metastable state can be transformed into the stable ordered state by density variations through variation of pressure or magnetic field. These variations produce a fluctuation energy $e_f$ which, when large enough, can cause a jump over the free energy barrier $f_B$. In vortex matter $e_f$ is related to the area under the M-H loop as the field is varied by h. This area, and thus $e_f$, increase monotonically but nonlinearly with h. If this field is varied n times with fixed h, then $e_f$ will increase linearly with n. With this basic idea, one can predict the effect of field variation h on various supercooled metastable states\cite{21}. We show, in fig. 2, three points in $(T,P)$ space where supercooled states are produced by lowering T at constant field. It follows that if $h_0$ is the lowest field excursion (with $n = 1$) for which the metastable state is transformed into a stable state, then $h_0$ will be smallest for point 1, and largest for point 3. Further if one uses a field variation $h_i$ which is lower than the smallest $h_0$, but makes repeated excursions until the stable state is formed after $n_0$ such field excursions, then it follows that $n_0$ will be smallest for point 1 and largest for point 3.

The predictions made above are qualitative and based on general arguments\cite{20, 21}; such predictions can be made for various possible paths of crossing the $T_C(P)$ line.

We have experimentally confirmed most of the predictions stated above with the PE in CeRu$_2$ as our paradigm FOT\cite{22}.

**HINDERED KINETICS AND KINETIC METASTABILITIES.**

The experimental confirmation of a FOT involves measurement of a volume discontinuity, also of a latent heat, and of these two satisfying the Clausius-Clapeyron equation. For vortex matter in CeRu$_2$ the discontinuity in vortex volume was observed by us\cite{19} but was tedious because we were extracting equilibrium magnetisation from hysteretic M-H curves\cite{23}. The latent heat has so far not been measurable, and hysteresis was invoked\cite{3, 10, 11} as a signature of an FOT. We have made predictions on path-dependence of metastabilities associated with an FOT, and these have also been observed. We must recognise that while we have advanced our understanding of metastabilities associated with FOTs, metastability can also
be kinetic in origin. We wish to now address this and pose some questions.

Glasses are known to be metastable, but differ significantly from supercooled liquids\[24\]. The diffusivity of a supercooled liquid does not drop suddenly below $T_C$; its diffusivity is large enough to permit it to explore configuration space on laboratory timescales. The ergodic hypothesis is valid, entropy is a valid concept and free energy can be defined, permitting the arguments we made in Section 2. A glass on the other hand is characterised by low diffusivity and hindered kinetics (with a viscosity greater than $10^{13}$ poise). It sits in a local minimum of only the energy landscape and not of the free energy, and is non-ergodic\[24\]. The low diffusivity of a glass causes metastabilities; the metastabilities are associated with hindered kinetics and not with local minima in free energy. Hindered kinetics (with kinetic hysteresis) will be seen wherever diffusivities are low, examples are critical slowing down near a second order phase transition and, closer home, M-H hysteresis in hard superconductors where the pinning, or hindered kinetics, of vortices prevents decay of shielding currents (Bean’s critical state model). Does a metastability induced by hindered kinetics also depend on the path followed in $(T,P)$ space? If the metastability is due to reduced diffusivity, then naïve arguments suggest that the metastability will be more persistent when larger motions (of particles in configuration space) are involved. And larger motions are involved when density is varied, rather than when temperature is varied. For the case of vortex matter, a much larger rearrangement of vortex structure is involved when we reach an $(H,T)$ point by varying field isothermally, than when we reach that point by varying temperature at constant field. Hysteresis would thus be lower in the field-cooled case, for hard superconductors, than in the case of isothermal field variation. This is consistent with observations\[25\], and with predictions of the Bean’s critical state model\[26\]. It is also well known that Bitter patterns generally show an almost disorder-free vortex lattice on reducing $T$ in constant $H$, in striking contrast to the case when $H$ is reduced in constant $T$. We thus conclude, with our naive arguments, that the path-dependence of metastability associated with hindered kinetics may be opposite to the case of metastability associated with a FOT.

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[1] G. Blatter, Physica C 282-287 19 (1997).
[2] U. Welp et. al., Phys Rev Lett 76 4809 (1996).
[3] E. Zeldov et. al., Nature 375 373 (1995).
[4] A. Schilling et. al., Nature 382 791 (1996).
[5] P. Fulde and R. A. Ferrel, Phys. Rev. 135A 550 (1964).
[6] A. I. Larkin and V. N. Ovchinnikov, Sov Phys JETP 20 762 (1965).
[7] L. W. Gruenberg and L. Gunther, Phys Rev Lett 16 996 (1966).
[8] S. Takahashi et. al., Physica C 263 30 (1996).
[9] R. Modler et. al., Phys Rev Lett 76 1292 (1996).
[10] K. Kadowaki et. al., Phys Rev B 54 462 (1996).
[11] S. B. Roy and P. Chaddah, Physica C 273 120 (1996).
[12] K. B. Blageev et. al., Phys. Rev. Lett. 82 133 (1999); W. E. Pickett et. al., Phys. Rev. Lett. 83 3713 (1999).
[13] S. B. Roy and P. Chaddah, Pramana-J. Phys. 53 659 (1999).
[14] P. Chaddah and S. B. Roy, Bull. Mat. Sc. 22 275 (1999).
[15] K. Huang, Statistical Mechanics (Wiley Eastern, New Delhi,1975) page 37.
[16] P. M. Chaikin and T. C. Lubensky, Principles of Condensed Matter Physics (Cambridge University Press, Cambridge, 1995) Chapter 4.
[17] P. G. Debenedetti, Metastable Liquids (Princeton University Press,1996); H. E. Stanley, Pramana-J. Phys 53 53 (1999).
[18] S. B. Roy and P. Chaddah, Physica C 279 70 (1997); S. B. Roy et. al., Physica C 304 43 (1998), 308 312 (1998).
[19] S. B. Roy and P. Chaddah, J. Phys. Cond. Mat. 9 L625 (1997); S. B. Roy et. al., ibid 10 4885 (1998), 10 8327 (1998).
[20] P. Chaddah and S. B. Roy, Phys. Rev. B 60 11926 (1999).
[21] P. Chaddah and S. B. Roy, submitted to Pramana - J. Phys.; also available at http://xxx.lanl.gov with number cond-mat (9910437).
[22] S. Chaudhary et. al., (to be published).
[23] P. Chaddah et. al., Phys. Rev. B 59 8440 (1999).
[24] F. H. Stillinger, Science 267 1935 (1995); J. Chem. Phys. 88 7818 (1988).

[25] K. A. Muller, M. Takashige and J. G. Bednorz, Phys. Rev. Lett. 58 1143 (1987).

[26] G. Ravikumar and P. Chaddah, Pramana - J. Phys. 31 L141 (1988).
Figure Captions

Fig. 1: We show schematic free energy curves for (a) $T = T^{**}$, (b) $T_C < T < T^{* *}$, (c) $T = T_C$, (d) $T^* < T < T_C$, and (e) $T = T^*$.

Fig. 2: We show a schematic of the phase diagram with supercooled states at 1, 2, and 3 obtained by lowering T in constant field (or ‘pressure’).
Supercooled region

$P (or \ H)$

$T_c(P)$

$T^*(P)$

$T$