Supercooling across first-order phase transitions induced by density variation

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We extend the standard treatment of supercooling across a first-order phase transition to consider the case when both temperature (T) and pressure (p) are varied. While the limit of metastability is independent of the path followed in (p,T) space, we shall argue that the observable region of metastability will depend on this path. We make comparisons between the observable region of metastability when (i) p is varied monotonically at constant T, and (ii) when small oscillations in p (at constant T) are also introduced, with the limiting region of metastability observable when only T is varied. [S0163-1829(99)03442-6]

A general phenomenon associated with first-order phase transitions is the presence of hysteresis in cycling through the transition. This results in supercooling of the high-temperature phase below the thermodynamic transition temperature T_C, and supercooled water is an extensively studied example.[1] Even though the inequality between the free energies of the two phases changes sign at T_C, the high-temperature phase is stable against small fluctuations until a lower temperature T^* is reached; below T^*, it is unstable against infinitesimal fluctuations.[2] While cooling the system through T_C, the low-temperature ordered phase may actually form at some temperature T_0 satisfying $T_C \geqslant T_0 \geqslant T^*$, with the region of metastability (T_C–T_0) depending on the fluctuation energy in the disordered phase.[2] There exists the analogous phenomenon of superheating which is dictated by the fluctuation energy in the ordered phase. Supercooling and superheating are usually discussed with temperature as the experimental control variable. This phase-transition line can also be crossed by varying another control parameter, viz. density. (Density can be varied by varying pressure, or in the case of vortex matter, by varying magnetic field. In this paper we use pressure as a generic term for both these experimental situations.) 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.[3–5] In this paper we follow the standard treatment[2] of supercooling across a first-order transition and consider the case when both temperature and pressure are varied to cross the phase boundary. While the limit of metastability is dictated by the line $T^*(p)$ independent of the path followed in (p,T) space, we shall argue that the actual region of metastability dictated by $T_0(p)$ does depend on the path followed in (p,T) space. In particular, the region of metastability is narrower when only p is varied compared to that when only T is varied. Furthermore, oscillations of the pressure p performed above $T^*(p)$ line can induce the supercooled metastable phase to transform to the stable ordered phase. As we shall argue, while supercooling all the way to T^* is possible when only T is varied if there are no fluctuations, the very procedure of varying p introduces fluctuations, making the supercooled state unstable at $T_0 > T^*$.

We shall first briefly outline the standard treatment[2] of supercooling across a first-order phase transition and then extend it to include density (or pressure) as a second control variable. We shall incorporate a pressure dependence in the expression for the free energy and discuss some features in the path dependence of $T_0(p)$ that are experimentally observable. A first-order transition occurs with varying temperature when the free-energy density can be expressed in terms of the order parameter S as

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

where w and u are positive and temperature independent, while r is temperature dependent and its sign changes at T^* (Ref. 2). [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.] T^* is the limit of metastability of the disordered ($S=0$) phase on cooling, T^{**} is the limit of metastability of the ordered ($S=S_C$) phase on heating, and T_C is the thermodynamic transition temperature at which $f(S=0)=f(S=S_C)$. We state below some standard results[2] relevant to our discussion:

(1) At $T=T_C$ there are two stable states with $f=0$, at $S=0$ and at $S=S_C=w/(2u)$. These are separated by an energy barrier peaking at $S=S_B=w/(4u)$, of height $f_B=w^4/(256u^3)$. These results are independent of any assumption about the temperature dependence of $r(T)$.

(2) If one assumes that $r(T)=a[T-T^*]$, where a is positive and temperature independent, then the limit of metastability is reached at $T^*=T_C-w^2/(2ua)$, at which temperature the barrier height falls (continuously) to zero. Similarly, the limit of metastability on heating is reached at $T^{**}=T_C+w^2/(16ua)$.

(3) Supercooling (or superheating) can persist until T^* (or T^{**}) only in the limit of infinitesimal fluctuations. The barrier height drops continuously as T is lowered below T_C, and in the presence of a fluctuation of energy e_f, supercooling will terminate at T_0 where the energy barrier is

$$f_B(T_0)\approx[e_f+k_BT_0]. \tag{2}$$

After stating some general results for metastability under a temperature-induced first-order transition, we now introduce pressure p as a second control variable. Since T_C is known to vary with p, one can construct a series of $f\ (p,T,S)$ curves as before (see Fig. 4.5.2 of Ref. 2), but for different fixed

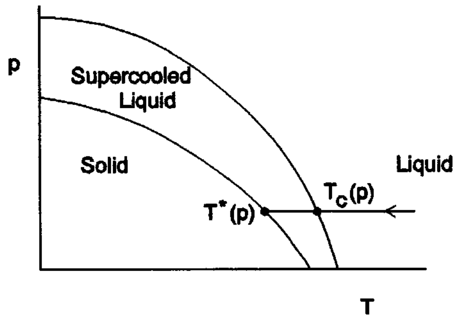

FIG. 1. We show a schematic of the melting line $T_C(p)$ assuming negative slope corresponding to liquid being more dense than solid. We also plot the limit of metastability $T^*(p)$ and we emphasize that $T_C - T^*$ rises as p rises.

values of p. The energy barrier f_B at any (p,T) point can be obtained as before by varying temperature with p fixed; supercooling the system along various (p,T) paths involves moving from an $f\ (p_1,T_1,S)$ curve to $f\ (p_2,T_2,S)$ curve in this multidimensional space.

We now incorporate a pressure dependence in the free-energy given by Eq. (1). The only T dependence is in the coefficient r, and we shall accordingly incorporate p dependence also in this coefficient only. Since $T^*(p) = T_C(p) - w^2/(2ua)$, the assumption of the coefficient a being independent of p implies that supercooling can persist for the same temperature difference at all p. This appears unphysical and we must therefore incorporate p dependence in the coefficient a. As we increase pressure or magnetic field to increase density, the interparticle potential energy will rise[6] at each S, and we add to the free energy a term $E_0(p)$ which rises with increasing p. This term is taken as independent of S. We then recognize that the phases with $S=0$ and S_C have different densities and there will be a small correction term which we incorporate in $a\ (p)$. The free energy is then written as

$$f(p,T,S) = E_0(p) + (1/2)a(p)[T - T^*(p)]S^2 - wS^3 + uS^4. \tag{3}$$

If the disordered $S=0$ phase has higher density (as in the water ice or vortex liquid-solid transitions[7]) then the energy change for the same increase in density (applied pressure or magnetic field) is more for the $S=0$ phase. This is accounted for by having $da(p)/dp < 0$. Similarly, if the ordered phase has higher density (as in most other liquid-solid transitions) then $da(p)/dp > 0$. Since the temperature window for the limit of supercooling in a constant pressure or magnetic-field phase transition is

$$T_C - T^*(p) = w^2/[2ua(p)], \tag{4}$$

we have the interesting consequence depicted in Fig. 1 that this window will increase with increasing pressure for the water-ice transition, and with increasing field in vortex-matter transitions. This window must decrease with increasing pressure for liquid-solid transitions in which the solid is more dense. These conclusions constitute a verifiable result.

We now consider an isothermal [with $T_1 = T^*(p_1)$] change of density in the disordered phase to cross the phase-transition line at (T_1,p_2). As the density is reduced further

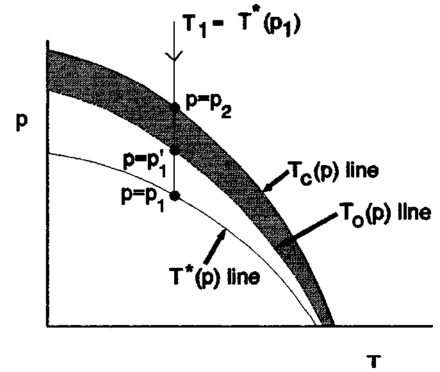

FIG. 2. If the density is reduced at constant temperature $T_1 = T^*(p)$, then supercooling will stop at a density $p' > p$, where p is the limit of metastability at T^*. Note also that $p' - p_1$ is larger at higher p or lower T_1. This is depicted in the figure by the dashed line moving further from $T^*(p)$ at higher p. The shaded region is the region of observable metastability when pressure is reduced isothermally.

(we assume without loss of generality that dp/dT is negative on the phase boundary), there is a barrier $f_B\ (p_2,T_1,S_B)$ and the system supercools in the metastable disordered state. The barrier will vanish only at p_1 since $T_1 = T^*\ (p_1)$ lies on the line defining the limit of metastability. We note from Eq. (3), however, that

$$f(p_2,T^*,0) - f(p_1,T^*,0) = E_0(p_2) - E_0(p_1), \tag{5}$$

which is finite. As the density changes and moving atoms encounter defects (or moving vortices get pinned and unpinned) a part of this energy given by Eq. (5) would be randomized and the system will have a fluctuation energy e_f because of the path traversed in (p,T) space. Because of this fluctuation energy, the metastable disordered state would become unstable even with a nonzero barrier before the density is reduced to p_1 [see Eq. (2)], and the metastable state transforms to the ordered state at $p_1' > p_1$. The variation of E_0 with density causes a source of fluctuations which is absent when T is varied at constant density. Thus, the metastable region is narrower if supercooling is attempted by varying density. We denote the observable limit of metastability, under an isothermal variation of density, by $T^0(p)$, and the point (T_1,p_1') lies on this line. We note that this $T^0(p)$ line lies above the $T^*(p)$ line, and this is depicted in Fig. 2. Furthermore, since $E_0\ (p_2) - E_0\ (p_1)$ is larger for larger p_2, the fluctuation energy rises if we increase p_2 or decrease the temperature T_1 of the isothermal scan. We conclude that $(p_1' - p_1)$ will rise with increasing p_2, and this is depicted in Fig. 2. We now continue with isothermal pressure reduction, but oscillate the pressure between p_1 and $p_1 - k$ before reducing it further. These oscillations cause dissipation of energy, and this dissipation in vortex matter is attributed to viscous motion of vortices and is well studied under the term ac losses.[8] The energy dissipation is easily measured in vortex matter through the integral $\int M \cdot dH$ over a closed cycle and depends in a nonlinear way on k, but increases linearly with number of oscillations (for fixed k). Since the oscillations in pressure add to the fluctuation energy e_f, Eq. (2) shows that the transition from the metastable to the ordered state will now occur at densities even higher than p_1', and this effect will increase as the number of oscillations is increased. This is another experimentally verifiable prediction of Eq. (3).

To conclude, we have extended the standard treatment of supercooling across a first-order phase transition to consider the case when both density and temperature are varied. When metastability or supercooling is seen on cooling at constant p, we predict how the window $T_C - T^*(p)$ will vary with p. We also predict that the observed region of metastability will be narrower if metastability is achieved by varying p at constant T, and that it can be made even narrower by causing small oscillations in density in the metastable phase.

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