Inverse Melting and the Emergence of Reentrant Phase in Physical Systems

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Abstract

Inverse melting (freezing) is the situation in which a solid melts (a liquid freezes) when the temperature of the system decreases (increases). It also concerns to the emergence of reentrant phase transition of a physical system. Here we overview these concepts and the corresponding phenomena, and discuss some generic features of these unusual phenomena.

I. INTRODUCTION

It seems universal that a more ordered state of any systems in thermal equilibrium will transform into a less ordered, or more disordered state as the temperature is increased. The most common cases in physical systems are that, with the increasing temperature, a solid/crystalline state melts into a liquid/fluid state, a ferromagnetic/antiferromagnetic state changes into a paramagnetic state, or a superfluid/superconducting state undergoes a transition into a normal state. However, it also really occurs that the less ordered phase can inversely "melts" into a high-temperature ordered phase, even such processes are relatively rare in the nature. Actually, this unusual and counterintuitive phenomenon does not violate the laws of thermodynamic, since the absolute measure for order and disorder is the entropy of the (isolated) system, which always increase (or at least does not decrease) with temperature. A usual quantity such as the order parameter, which has variant definition in different systems, is a measure that subjectively characterizes the degree of order of the system.

An interesting issue is how inverse melting, as described above, occurs as the temperature varies in the systems. This can happen if the so called "ordered" phase has more entropy than the "disordered" phase. For example, if in the liquid phase some of the degrees of freedom of the elementary constituents are frozen, inverse melting may occur from this phase to a more solidify phase with the gain of entropy by exciting these frozen degrees of freedom [1]. A possible scenario is that the instability of a low-temperature disordered state increase with temperature, and eventually at some critical temperature the low-lying excited or metastable state becomes the most stable one, undergoing an inverse phase transition. This may take place in a range of some physical parameters, such as pressure, chemical potential, the concentration of doped impurity in solid state system, or the coupling of interaction between particles. For example, the inverse melting from an amorphous phase to a crystalline phase has the general structure as shown in the "Tammann's universal phase diagram" (FIG. 1) discussed in [2].

Another interesting concept is the emergence of the reentrant phase, that is, one phase undergoes a transition followed by a return to its original phase as the temperature changes monotonically (keeping other relevant parameters of the systems unchanged). This phenomenon must accompany the inverse melting (or freezing) in the one phase boundary of the two transition points. Such disorder-order-disorder (or inverse) sequences of transition manifest the competition between different effects and mechanism that are usually opposite in determining the stabilities of the ground state. These two reentrant phase, though identical macroscopically, may have the disorder differently driven by, for example, the

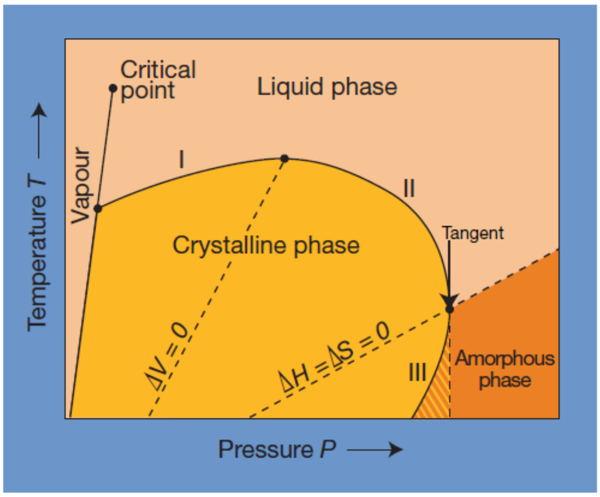

FIG. 1: Tammanns universal pressure and temperature phase diagram. Melting as usually observed occurs in regions I and II, whereas "inverse melting" occurs in region III [2].

thermal and quantum fluctuations.

In the next section, we demonstrate some physical systems that exhibit the phenomena of inverse melting and reentrant phase behavior.

II. EXPERIMENTAL EVIDENCES IN SOME PHYSICAL SYSTEM

A. Rochelle Salt

The Rochelle salt (sodium potassium tartrate dehydrate) which exhibits ferroelectric properties has two Curies points [3]. This material is paraelectric with an orthorhombic structure, and below - 18°C and above 24°C, and it is ferroelectric with a monoclinic structure between these two critical temperatures. Since the crystalline structure above the upper Curie point and below the lower Curie point is the same, this system characterizes a reentrant phase transition. The inverse melting occurs at the lower critical temperature, when the orthorhombic structure melts into the monoclinic one, which is less symmetric, as temperature increases.

B. Liquid Solutions

A liquid solution composed of α-cyclodextrine (αCD; the molecular structures is shown in the top part of FIG. 2), water, and 4-methypyridine(4MP) exhibits the phenomenon of

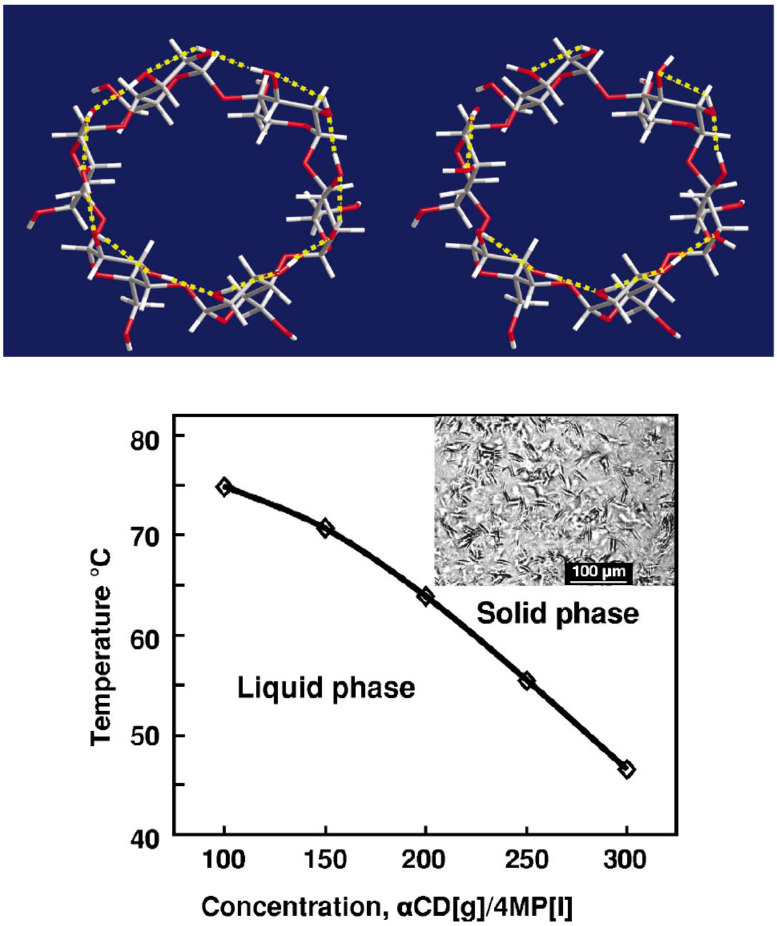

FIG. 2: Top: Molecular structures αCD: minimum energy structure with 12 intramolecular hydrogen bonds and structure in which 4 of the 12 hydrogen bonds are broken. Bottom: Temperature of solidification of αCD/4MP solutions as a function of αCD concentration. Inset: photomicrograph of the solid phase [4].

inverse freezing – a liquid -solid transitions upon heating [4]. Unlike some usual systems that also exhibit this phenomenon like polymerization, in which the chemical properties of the material changes irreversibly, the process of the transition observed in this relatively small and rigid molecules is reversible and more interesting. In the range of temperature between 45°C and 75°C, the molecular motions of this solution are slowed down such that the system tends to solidify and form a crystalline order. The transition temperature of the solidification varies with the change of concentration of (αCD) in 4MP (bottom part of FIG. 2). Out of this range of temperature the solution behaves as a homogeneous and transparent liquid. A rearrangement of hydrogen bonds among αCD-water-4MP that forms an ordered structure filled with liquid 4MP drives the appearance of the solid phase.

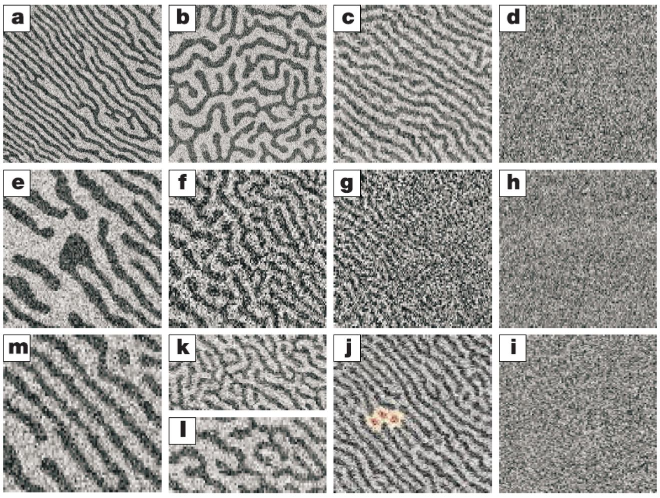

FIG. 3: The four phases in ultrathin f.c.c. Fe films. **a–d**, The effective temperature is increased (by decreasing the film thickness) from left to right;**e–h**, A fixed region of a film is imaged while the temperature is increased from e to h;**i–m**, A fixed region of a film is imaged while the temperature is lowered. The inverse freezing (or melting) process is seen in **b–c**, **f–g**, and **j–k** [5].

However, at lower temperature the establishment of intramolecular hydrogen bonds in αCD prevents the construction of this ordered structure formed by the network through intermolecular hydrogen bonds. The competition between these molecular interactions, which leads the subtle equilibrium of this system, characterizes this unusual type of phase transition upon heating.

C. Domain Patterns in Magnetic Thin Films

A reentrant phase transition also exists in an ultrathin face-centered-cubic (f.c.c.) Fe films on Cu(001), which are magnetized perpendicular to the film plane [5]. The magnetization of the films emerges as a non-uniform stripe domain patterns with opposite perpendicular magnetization. It was observed that, from scanning electronic microscopy imaging with polarization analysis (SEMPA), a more symmetric labyrinthine structure establishes in the film, as an intermediate phase adjacent between two less symmetric stripe phases. At an even higher temperature the magnetization vanishes, manifesting as the paramagnetic phase. FIG. 3 shows the evolution of these four distinct patterns in different temperatures. The stripe phase at higher temperature undergoes the inverse melting to a labyrinthine phase. The main microscopic mechanism of the transition from

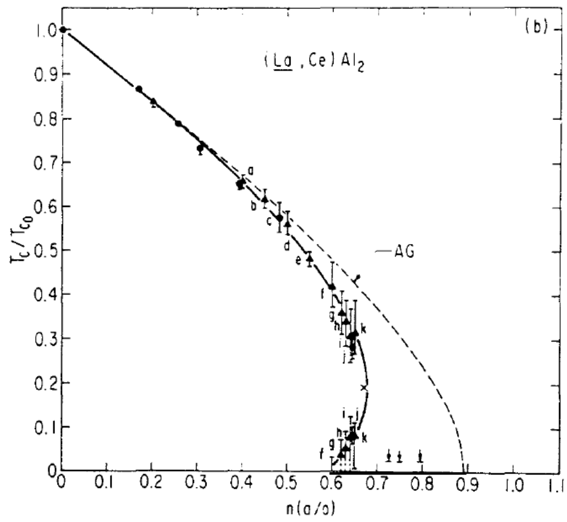

FIG. 4: Reduced transition temperature V.S. impurity concentration for the system of $(La,Ce)Al_2$ alloys [7].

the labyrinthine pattern to the re-entrant stripe pattern is led by knee-bend and bridge instabilities existing in the domain pattern. By emitting a segment into adjacent domain of opposite magnetization, these instabilities can straighten the labyrinthine pattern and thus allows for the required increase of the stripe density as the temperature is increased. The system provides some unpredicted geometrical features of the magnetic phase transition, which were not considered in mean-field arguments and should be significant for any type of stripe order.

D. Superconductors

The emergence of reentrant phase transition was also found in superconductors, associating an unusual superconducting-normal state transition in temperature. Some superconductors doped with magnetic impurities have the reentrant behavior that the system becomes superconducting at some critical temperature followed by a return to the normal state at another critical temperature (FIG. 4). The phase behavior of such "dirty" superconductors is attributed to the finite amount of impurity concentration that substantially change the bulk properties of a superconductor [6]. The competition between the magnetic effects due to impurities and superconductivity leads a more complicated mechanism (than the conventional one such as BCS theory) for transition between superconducting and normal state. Such magnetic effect might be the Kondo effect [7], or the long-range ordering of magnetic moments – which can be either ferromagnetic [8] or

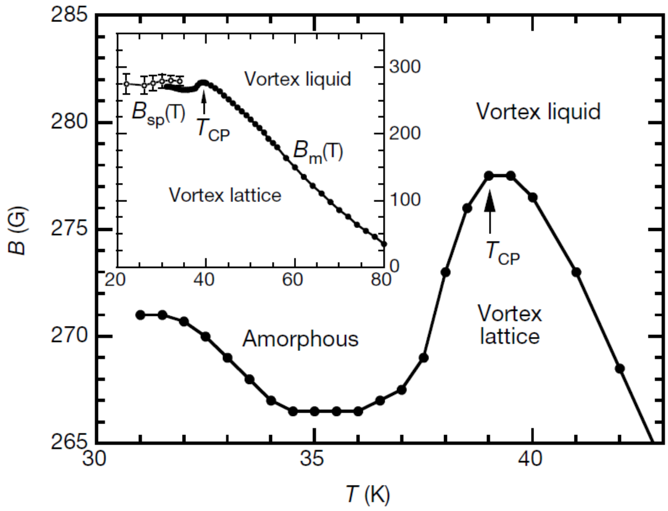

FIG. 5: The first-order transition line obtained in BSCCO crystal B. The inverse melting occurs at left slope of the main peak. Inset, the first-order $B_m(T)$ line (filled circles) along with the second magnetization peak line $B_{sp}(T)$ (open circles) over a wide temperature range [10].

antiferromagnetic [9] - of the ions existing in some compound materials, such as $ErRh_4B_4$ and $GdMo_6Se_8$.

Another example concerning the superconducting system is the inverse melting of a vortex lattice formed by magnetic by magnetic flux lines in a high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$ (BSCCO) [10]. From the use of a transverse a.c. field to achieve vortex equilibration by reducing the irreversible magnetization caused by vortex pinning , the therymodynamic evidence of this first-order inverse melting of the ordered lattice (Bragg glass) into a disordered amorphous vortex phase was observed as the temperature is decreased (FIG. 5). The transition from the lattice the liquid phase is not thermally driven, but is disorder-driven by pinning the flux line to impurities in the lattice at low temperature. The loss of elastic energy of the lattice is balanced by a gain in pinning energy, and thus the ordered lattice still has larger entropy than the low-temperature disordered phase. Since the ordered lattice has no dislocations and is structurally more ordered, the extra entropy must arise from additional degrees of freedom. It is also indicated that the disorder-driven transition should be a more general phenomenon and is apparently at the heart of the ubiquitous peak effect (of the melting transition line) in low-T_c superconductors [10].

III. THEORETICAL INVESTIGATION: A SIMPLE MODEL FOR INVERSE MELTING AND REENTRANT PHASE

In the previous section we review some experimental results for inverse melting and reentrant phase behavior in different physical systems. The corresponding theoretical explanations and models for Rochell salt [11, 12], the liquid solutions of αCD-water-4MP [13], the domain patterns in magnetic [14], reentrant superconductivity [6, 15], and vortex matter in high-T_c superconductor [16] have also been studied. There is also a statistical mechanical model for inverse melting proposed [17]. Here we introduce a simple model that exhibits the reentrant phase behavior, the two-dimensional random-bond Ising Model, which is a simple disordered spin model with frustration. Studies on this model show that reentrant behavior is generic whenever frustration is present in the model [18]. The Hamiltonian in this model is

$$H = -\sum_{\langle ij \rangle} J_{ij} s_i s_j, \tag{1}$$

with an $L \times L$ square toroidal grid [18] of Ising spins $\{s_i \in \pm 1\}$ and quenched nearest-neighbor random couplings J_{ij}. The random couplings $\{J_{ij}\}$ can be chosen from both discrete and continuous bond disorder:

$$P(J_{ij}) = p\delta(J_{ij} - J) + (1-p)\delta(J_{ij} + J), \tag{2}$$

as a bimodal distribution, and

$$P(J_{ij}) = (2\pi \tilde{J}_{ij}^2)^{-1/2} \exp[-(J_{ij} - J)^2/(2\tilde{J}^2)], \tag{3}$$

as a Gaussian distribution. The phase diagrams with the critical temperatures varying with the respective disorder strength parameters $q = 1 - p$ and $r = \tilde{J}/J$ are shown in FIG. 6. In both cases we can see the reentrant phase behavior in a range of the disorder strength parameters.

In this model, the size and energy scale of the ground-state ferromagnetic domains are set by the disorder strength. Within a range of this parameter the ferromagnetic ordering dominates in zero temperature. As the disorder increases the ground state becomes paramagnetic, but for a range of parameters the ferromagnetic domains coupled strongly enough in the low-lying excitations, resulting the reentrant behavior in the system. It might be a generic feature that the disorder and frustration are crucial for emergence of the reentrant phase.

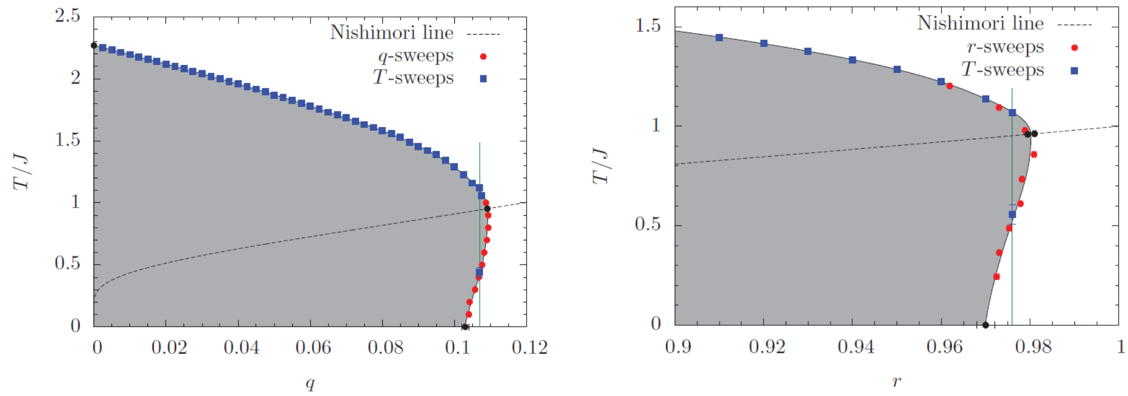

FIG. 6: Phase diagrams of the two-dimensional random-bond Ising model with the bimodal distribution (left part) and with the Gaussian distribution (right part).The shaded region is ferromagnetic, while the white region is paramagnetic. The reentrant phase behavior occurs in a range of the disorder strength parameters [18].

IV. DISCUSSION AND SUMMARY

In this essay we discuss the concepts of an unusual process – the occurrence of inverse melting (or freezing) and the emergence of the reentrant phase in physical systems. We also demonstrate the corresponding phenomena in some materials: the ferroelectric-paraelectric transitions in Rochell salt, the liquid-solid transition in liquid solutions, the evolutions of domain patterns with temperature in magnetic thin films, the reentrant superconductivity, and vortex matter transformations in high-T_c superconductors. Through these experimental results we can see some generic features of these counterintuitive phenomena. The underlying mechanisms are usually led by the competition between various effects - which are usually opposite in determining the stabilities of the ground state - in different temperature. We then investigate a simple model, the two-dimensional random-bond Ising Model, to study the reentrant behavior of the paramagnetic phases. It explicitly displays that the disorder and frustration presented in this model are responsible for reentrant phase transitions. This provides a basic framework and idea to explore more relevant phenomena in the nature.

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