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A New Perspective on the Kauzmann Entropy Paradox: A Four-Dimensional Crystal/Glass Quantum Critical Point

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Abstract: In this article, a new perspective on the Kauzmann point is presented. We model the solidifying liquid by a quaternion orientational order parameter and find that the Kauzmann point is analogous to a quantum critical point. The “ideal glass transition” that occurs at the Kauzmann temperature is the point at which the configurational entropy of an undercooled metastable liquid equals that of its crystalline counterpart. We identify this point as a first order quantum critical point. We suggest that this quantum critical point belongs to quaternion ordered systems that exist in four- and three-dimensions. This “Kauzmann quantum critical point” can be considered to be a higher-dimensional analogue to the superfluid-to-Mott insulator quantum phase transition which occurs in two- and one-dimensional complex ordered systems. Such quantum critical points are driven by tuning a non-thermal frustration parameter, and result due to characteristic softening of a ‘Higgs’ type mode that corresponds to amplitude fluctuations of the order parameter. The first-order nature of the finite temperature Kauzmann quantum critical point is seen as a consequence of the discrete change of the topology of the ground state manifold that applies to crystalline and non-crystalline solid states.

1. Introduction

The nature of the glass transition is widely thought to be one of the most challenging problems in condensed matter physics [1–4]. Despite their ubiquity, a fundamental understanding of amorphous solids and the glass transition has yet to be obtained. This is in stark contrast to our knowledge of crystalline solids, which result by first-order phase transitions and in which phonons (collective Nambu-Goldstone modes) develop to transport thermal energy. Unlike crystallization, glass formation is non-equilibrium and the glass transition results as an undercooled liquid breaks ergodicity to become a rigid solid.

The glass transition is highly dependent on the cooling rate; with a slower cooling rate, an undercooled liquid may remain ergodic to lower temperatures. As the temperature of an undercooled liquid is decreased, the difference in entropy between the liquid and crystalline solid phase decreases. Because the entropy of undercooled fluids declines faster with temperature than does crystal entropy, this results in an entropy paradox at a certain finite temperature (Kauzmann temperature $T_K$) that may be achieved in the limit of an infinitely slow cooling rate [5–7]. An “ideal glass,” that forms at the Kauzmann temperature, has a configurational entropy that matches its crystalline counterpart. This is known in the literature as the Kauzmann entropy paradox [5–7]. “Ideal glass transitions” have never been obtained in the laboratory, as any real glass transition occurs at a temperature higher than $T_K$ and is caused by kinetic constraints that are responsible for a loss of ergodicity [8]. Yet, the physics underlying the Kauzmann entropy paradox presents an interesting problem in condensed matter physics.
The objective of this article is to describe the nature of formation of crystalline solids from the liquid state, and the origin of the Kauzmann entropy paradox, by the application of a quaternion orientational order parameter. This approach makes use of the principles of spontaneous symmetry breaking and of topological-ordering, that are known to play key roles in our understanding of condensed matter. Analogies between solidification and the formation of complex ordered states of matter, in two- and one-dimensions, are developed in order to frame the Kauzmann point as a quantum critical point (QCP) that exists to separate crystalline and glassy solid states.

The topological properties of the free energy functions that apply to crystalline and glassy solids are compared, and the roles of the two types of fundamental excitations: massless phase modes (Nambu-Goldstone) and a massive amplitude mode (‘Higgs’) are discussed. These considerations enable the characterization of the “ideal glass transition,” at the finite Kauzmann temperature, as a first-order QCP similar to the second-order superfluid/Mott-insulator quantum phase transition (QPT) that occurs in two- and one-dimensions [9].

2. Crystalline-to-Glass First-Order Quantum Critical Point and the Kauzmann Entropy Paradox

Quantum phase transitions [10] exist for $O(N)$ quantum rotor models of $N-$vector ordered systems, that exist in $N$ or $N-1$ dimensions, which are constructed by taking into account both potential and kinetic energy terms. Such QPTs [10] are driven by tuning a dimensionless frustration parameter ($g$), that is a measure of the ratio of kinetic energy to potential energy. $O(2)$ quantum rotor models have been applied extensively to understand the nature of the superfluid/Mott-insulator QPT in two- and one-dimensions [9].

In complex ordered systems, an order parameter with $N = 2$ components develops. In two- and one-dimensions, such complex ordered systems are described using $O(2)$ quantum rotor models that give the dynamics of the complex order parameter ($\Psi = |\Psi|e^{i\theta}$) near a QPT between phase-coherent superfluid ($|\Psi| > 0$) and phase-incoherent Mott-insulator ($|\Psi| = 0$) states. In superfluids, the free energy function has the form of a conventional ‘Mexican hat’ (Figure 1A) where the order parameter has a non-zero value at its basin. In complex ordered systems that exist in 2D/1D, as opposed to 3D, phase-coherent superfluid ground states are achieved via a Kosterlitz-Thouless topological-ordering transition in which vortex defects and anti-defects form bound states (Figure 2). In the classical limit, i.e., in absence of kinetic energy effects (frustration), the scalar phase angle $\theta$ acquires a definite value below the Kosterlitz-Thouless transition through breaking of rotational symmetry – and the superfluid ground state is perfectly phase-coherent.

Around the symmetry-broken ground state, there are two mode types: a massless Nambu-Goldstone mode related to fluctuations in the scalar phase angle $\theta$ and a massive ‘Higgs’ mode related to amplitude variations in $\Psi$. As the amount of frustration reaches a critical value, in the vicinity of the QPT to the phase-incoherent Mott-insulator, there is a characteristic softening of the excitation gap or mass of the Higgs amplitude mode [9]. This softening transforms the free energy into a function with a minimum at $|\Psi| = 0$ in the phase-incoherent Mott-insulating state [9] (Figure 1B).

The order of the quantum phase transition, that belongs to an $O(N)$ quantum rotor model, in $N$ or $N-1$ dimensions, can be discerned by noting changes in the topological properties of the free energy function in its vicinity. In the case of the superfluid/Mott-insulator QPT, the topology of the ‘Mexican hat’ that applies to the superfluid is circular and the free energy of the Mott-insulator retains $U(1) \cong S^1$ symmetry at the origin. Thus, the superfluid/Mott-insulator QPT is continuous and is therefore of second-order. Such a second-order QPT occurs at zero Kelvin (Figure 3A), and describes a change in the ground state as a result of quantum fluctuations arising from the Heisenberg uncertainty principle [10].
Figure 1. (A) The ‘Mexican hat’ free energy function of complex ordered systems whose complex order parameter has the form $\Psi = |\Psi|e^{i\theta}$. In the phase-coherent superfluid phase, $|\Psi| > 0$ and a massless Nambu-Goldstone and a massive Higgs modes arise. (B) On approaching the two-dimensional superfluid/Mott insulator QPT, at a critical value of frustration $g_C$, the free energy function transforms to one with a minimum at $|\Psi| = 0$. [Reproduced from Ref. [9]]

Figure 2. Classical 2D/1D $O(2)$ rotor model. (A) An abundance of misorientational fluctuations develops below the bulk Bose-Einstein condensation temperature ($T_{BEC}$), and may be discretized as a plasma of isolated point defects and anti-defects. (B) As the temperature is lowered below the Kosterlitz-Thouless transition temperature ($T_{KT}$), complementary defects/anti-defects begin to form bound pairs. (C) As the temperature approaches 0 K, defects and anti-defects that comprise bound states come together and annihilate. In the absence of frustration, no signed defects persist to the ground state that is perfectly phase-coherent.

In the same way that the degree of order in superfluids (phase-coherent) is described by a complex order parameter, it has recently been proposed by the authors that orientational-order in crystalline solids may be described by a quaternion order parameter [11,12]. The quaternion orientational order parameter that is adopted has the form: $\Psi = |\Psi|e^{i\theta}$ where $\theta \in [0, \pi]$ is a rotation angle and $\hat{n}$ is a unit-length vector quaternion ($\hat{n}^2 = -1$) that acts as the axis of rotation. This orientational order parameter depends upon three scalar phase angle parameters ($\theta, \theta_1 \in [0, \pi]$ and $\theta_2 \in [0, 2\pi]$) and a single amplitude degree of freedom ($|\psi|$).

In four- and three-dimensions, $O(4)$ quantum rotor models apply to mathematically model quaternion ordered systems – as these may be considered to be “restricted dimensions” for quaternions in the Hohenberg-Mermin-Wagner sense [13–15]. When applied to the solidification problem, the quantum critical point that belongs to the $O(4)$ quantum rotor model is anticipated to separate crystalline (i.e., orientationally-ordered) and non-crystalline (i.e., orientationally-disordered) solids.
Crystalline solids are anticipated to develop as a result of a defect-driven topological-ordering transition [12,16], just as the Kosterlitz-Thouless mechanism [17,18] allows for the realization of superfluids in 2D/1D. Just as first homotopy group defects are available to complex ordered systems (i.e., $\pi_1(S^1)$ vortices), third homotopy group defects are available to quaternion ordered systems ($\pi_3(S^3)$). Vortices are points in two-dimensions (complex plane) and third homotopy group defects are points in four-dimensions (quaternion plane). In these “restricted dimensions” (Hohenberg-Mermin-Wagner theorem [13–15]), defect binding via a Kosterlitz-Thouless mechanism is necessary to prevent the mobility of misorientational fluctuations such that phase-coherency or long-range orientational-order may be obtained.

In addition to third homotopy group defects, closed-loop (fundamental group) defects [19–21] exist below the melting temperature as a consequence of the discrete orientational-order in clustered undercooled fluids. Such defects are known as disclinations. Just as complementary third homotopy group point defects form bound pairs on crystallization, disclinations of equal and opposite sign come together to form dislocations [22–25]. In perfect crystals, at absolute zero temperature, definite values for the set of three scalar phase angle parameters that define the quaternion order parameter are obtained as components of bound pair excitations come together and annihilate.

In the presence of finite frustration effects, on approaching the quantum critical point from the limit of a perfect crystal, crystalline solid states may form in which local orientational-order is incompatible with long-range crystallographic packing. Examples of such structures are topologically close-packed Frank-Kasper crystalline solids [27,28], in which geometric frustration [29,30] prevents the development of long-range icosahedral orientational-order. Such geometrically frustrated crystalline structures (e.g., Frank-Kasper) are stabilized in the ground state by a periodic arrangement of signed topological defects. In particular, the frustration-induced signed disclination lines that are present carry negative curvature and form what is known as a “major skeleton network” (Figure 4). An entangled array of negative disclination lines is an attractive model for the structure of glasses [21,29], that form above a critical amount of geometrical frustration. Just as topologically close-packed crystalline solids may be viewed as analogous to 2D/1D superfluids with a finite amount of frustration, orientationally-disordered glasses are similar to the phase-incoherent Mott-insulator state [9].

**Figure 3.** (A) Complex ordered systems ($N = 2$) that exist in 2D/1D are mathematically described using O(2) quantum rotor models, that admit a second-order QPT at absolute zero temperature [26]. This is the superfluid/Mott-insulator QPT [9]. (B) Solidification processes in four- and three-dimensions, as characterized by a quaternion orientational order parameter ($N = 4$), are described using O(4) quantum rotor models. Such O(4) quantum rotor models admit a QCP that is first-order. This may be identified with the “ideal glass transition,” that occurs at a finite Kauzmann [5] temperature.
In geometrically-frustrated crystalline structures, i.e., topologically close-packed, frustration-induced topological defects form a periodic arrangement. The ordered arrangement of negative wedge disclinations \[27,28\] is known as the “major skeleton network.” Signed third homotopy group defects also form a periodic arrangement, in geometrically-frustrated crystalline solids, but are not visible because of their nature as points in four-dimensions. [Reproduced from Ref. [31]]

In crystalline solids, the order parameter manifold has the topology of a three-dimensional torus \(T^3 \cong S^1 \times S^1 \times S^1\) that accommodates periodic boundary conditions. This can be viewed as a higher-dimensional, quaternionic, version of the ‘Mexican hat’ of superfluids (Figure 1A). Around the symmetry-broken crystalline ground state: three massless phonon modes (Nambu-Goldstone) and a massive mode (‘Higgs’), related to the amplitude variations in \(\Psi\), exist.

Like the 2D/1D superfluid/Mott-insulator QPT \[9\], softening of the excitation gap of the amplitude mode is anticipated as frustration is increased to approach the QCP that belongs to \(O(4)\) quantum rotor models in 4D/3D. This softening transforms the order parameter manifold into a function with a minimum at \(|\Psi| = 0\), at the QCP, which retains \(SU(2)/H'\) symmetry at the origin (where \(H'\) is the binary polyhedral group of preferred local orientational order \(H \in SO(3)\), and \(SU(2) \cong S^3\)).

Owing to the discontinuous change in the genus topological invariant of the ground state manifold that applies to crystalline and glassy solids, the frustration-induced QCP is first-order and thereby occurs at a finite temperature (Figure 3B). When considering solidification processes, this first-order QCP may be identified as the Kauzmann point \([5]\) that occurs at the finite Kauzmann temperature (“ideal glass transition”). The Kauzmann entropy paradox that occurs at the Kauzmann QCP, where the configurational entropy of an undercooled liquid and its crystalline counterpart are equal, is physically acceptable at finite temperatures but would not be so at the absolute zero of temperature. Although the finite temperature nature of the “ideal glass transition” is well-understood based upon thermodynamic principles, this topological interpretation of its first-order nature is novel.

3. Conclusions and Outlook

The abundance of literature that exists on the nature of both the real and the “ideal glass transition” clearly reflects the importance of the free energy landscape in providing a qualitative explanation of the phenomenon. In this article, we have suggested that crystallization and glass formation can be understood within a unified framework by the application of a four-dimensional quaternion orientational order parameter. As a generalization of the superfluid/Mott-insulator quantum phase transition (QPT) in two- or one-dimensions, a quantum critical point (QCP) is anticipated for quaternion ordered systems that exist in four- or three-dimensions. This QCP has been identified with the “ideal glass transition,” that occurs at the finite Kauzmann temperature.

The first-order nature of the Kauzmann QCP, at which the Kauzmann entropy paradox may be realized, has been determined by accounting for the discrete change in the topology of the
ground state manifold that applies to crystalline (orientationally-ordered) and non-crystalline (orientationally-disordered) solid states. Just as in the case of the superfluid/Mott-insulator QPT, the ground state manifold is anticipated to become modified due to characteristic softening of the amplitude mode (‘Higgs’) on approaching the Kauzmann QCP from the limit of a perfect crystal.

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