General Mechanism for a Positive Temperature Entropy Crisis in Stationary Metastable States: Thermodynamic Necessity and Confirmation by Exact calculations

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Abstract

We introduce the concept of stationary metastable states (SMS’s), and give a prescription to study it using a restricted partition function formalism. This requires introducing a continuous entropy function \( S(E) \) even for a finite system, a standard practice in the literature though never clearly stated, so that it can be differentiated. The formalism ensures that SMS free energy exists all the way to \( T = 0 \), and remains stable. We introduce the concept of the reality condition, according to which the entropy \( S(T) \) of a set of coupled degrees of freedom must be non-negative. The entropy crisis, which does not affect stability, is identified as the violation of the reality condition. We identify and validate rigorously, using general thermodynamic arguments, the following general thermodynamic mechanism behind the entropy crisis in SMS. The free energy \( F_{\text{dis}}(T) \) of any SMS must be equal to the \( T = 0 \) crystal free energy \( E_0 \) at two different temperatures \( T = 0 \), and \( T = T_{\text{eq}} > 0 \). Thus, the stability requires \( F_{\text{dis}}(T) \) to possess a maximum at an intermediate but a strictly positive temperature \( T_K \), where the energy is \( E = E_K \). The SMS branch below \( T_K \) gives the entropy crisis and must be replaced by hand by an ideal glass free energy of constant energy \( E_K \), and vanishing entropy. Hence, \( T_K > 0 \) represents the Kauzmann temperature. The ideal glass energy \( E_K \) is higher than the crystal energy \( E_0 \) at absolute zero, which is in agreement with the experimental fact that the extrapolated energy of a real glass at \( T = 0 \) is higher than its \( T = 0 \) crystal energy. We confirm the general predictions by two exact calculations, one of which is not mean-field. The calculations clearly show that the notion of SMS is not only not vacuous, but also not a consequence of a mean-field analysis. They also show that certain folklore cannot be substantiated.
1 Introduction

Glass transition is a ubiquitous phenomenon\(^1\)\(^2\), believed to occur in a supercooled liquid (SCL), which is one of the metastable states in Nature, and has been investigated for at least over eight decades since the earliest works of Nernst\(^3\) and Simon\(^4\). Despite this, a complete understanding of the transition itself and related issues is still far from complete, although major progress has been made recently\(^5\)\(^6\)\(^7\)\(^8\). Theoretical and experimental investigations invariably require applying (time-independent) thermodynamics to SCL to extract quantities like the entropy. This presumes, as we do here, that there exists a stationary limit of the metastable SCL state (SMS) under infinitely slow cooling in which the crystal (CR) is forbidden from nucleating\(^9\). We further assume that the SCL free energy can be defined, at least mathematically (see below for details), all the way down to absolute zero, which may not always be possible. It was discovered recently that under some conditions, SCL free energy can terminate in a spinodal at a non-zero temperature as we lower the temperature\(^8\).

Experimentally, the SCL configurational entropy exhibits a rapid drop near a temperature \(\simeq\) two-thirds of the melting temperature \(T_M\)\(^1\)\(^2\). It is found that the smooth low-temperature extrapolation of the measured excess entropy \(S_{\text{ex}}(T) \equiv S_{\text{SCL}}(T) - S_{\text{CR}}(T)\) becomes negative\(^1\) below a non-zero temperature. Since it is hard to imagine CR, being more ordered, having a larger entropy than SCL, Kauzmann suggested that something like a glass transition must intervene to avoid this entropy crisis, known commonly as the Kauzmann paradox \((S_{\text{ex}}(T) < 0)\)\(^1\), at some positive temperature. There are several computational\(^6\) and theoretical\(^7\)\(^8\)\(^10\)\(^12\) results clearly demonstrating the existence of some kind of entropy crisis.

It should be stressed that there is no thermodynamic requirement for \(S_{\text{ex}}(T)\) to be non-negative. There are physical systems like He\(^4\) in which \(S_{\text{ex}}(T)\) can become negative at low temperatures. A recent exact calculation on a classical system\(^7\) clearly demonstrates a negative \(S_{\text{ex}}(T)\) at low temperatures. If there is any hope of finding a thermodynamic basis for the glass transition, we must look for a condition for the glass transition that is dictated by thermodynamics. Thus, in the following, we replace \(S_{\text{ex}}(T)\) by the entropy \(S(T)\), such as the configurational entropy, which represents the natural log of the number of microstates \(W(E)\), where \(E\) is the average energy at that temperature. Consequently, a state with negative entropy is impossible to observe in Nature. The violation of the reality condition \(S(T) \geq 0\) signifies a genuine or absolute entropy crisis in Nature. We will interpret the entropy crisis in this work to signify the reality condition violation \(S(T) < 0\), and denote the temperature by \(T_K\), the Kauzmann temperature, when the violation begins as the temperature is reduced.

It is widely recognized that \(T_K\) is a theoretical point and not accessible by experiment. However, its accessibility in itself is not important if its usage helps us understand or explain glassy behavior. It is well known that absolute zero is inaccessible; yet the study of a statistical model at \(T = 0\) is a time-honored first
step to study the physics of the model at higher temperatures. The concept of a Kauzmann temperature enables us to explain many glassy behavior. For example, the existence of the entropy crisis at a non-zero temperature is conceptually necessary for the observed Vogel-Fulcher behavior in fragile systems. Its importance cannot be denied just because it is experimentally inaccessible. A majority of the experts in the field continues to find the Kauzmann temperature to be an extremely useful concept. The most important consequence of a positive $T_K$ is that there is a lower limit to supercooling before an experimental glass transition must intervene, and this lower limit is not absolute zero. This is an extremely useful information for experimentalists who are interested in investigating glassy behavior.

The following two experimental observations play a very important role in our understanding of the glass transition:

(Expt1) The heat capacity of the glassy state can be substantially different from that of the corresponding crystal at the same temperature\(^{[14]}\).

(Expt2) The energy of the glassy state ($E_K$) after extrapolation to absolute zero is higher than that of the CR energy $E_0$\(^{[1],[2]}\).

Based on these observations, we have recently proposed\(^{[7],[8]}\) a mechanism behind the entropy crisis and the ideal glass transition in the SMS of a system of long polymers. The proposed mechanism is as follows.

**Entropy Crisis Mechanism** Since $E_K > E_0$, the SMS free energy rises rapidly below the melting temperature $T_M$ as the system is cooled and crosses the $(T = 0)−CR$ free energy $E_0$ at some positive temperature $0 < T_{eq} < T_M$. The SMS free energy again equals $E_0$ at $T = 0$. Therefore, it must go through a maximum at $0 < T_K < T_{eq}$, at which the entropy of the system vanishes. Since negative entropy below $T_K$ is not possible for physical states, the SMS below $T_K$ is replaced by an ideal glass with a constant free energy $E_K$, and zero entropy and heat capacity.

Since the above two experimental observations are the main ingredients for the proposed mechanism, it appears likely that the mechanism is common to all glass forming systems with metastability, and not just restricted to long polymers. If true, this will suggest that the above mechanism is a generic root cause of the entropy crisis at a positive temperature in all systems in which glasses are formed by cooling their metastable states.

However, the situation has become very confusing, as there have appeared several recent arguments\(^{[15],[16],[17],[18]}\) against the existence of the entropy crisis. These arguments contradict many exact calculations\(^{[7],[8],[10],[11],[12]}\) and simulations\(^{[6]}\) that clearly establish a positive-temperature entropy crisis. We should also mention classical real gases, like the van der Waals gas, or the classical ideal gas that are known to give entropy crisis at positive temperatures\(^{[13]}\). It is, therefore, extremely important to clarify the issue, which we do by proving the general validity of the above mechanism behind all glass formation in metastable states. Two important aspects in the mechanism require general justification\(^{[19]}\):

(M1) The SMS free energy, obtained by mathematical continuation of the disordered equilibrium state below the melting temperature, and the CR free
energy are the same at absolute zero.

(M2) The temperature $T_K$ when the entropy crisis occurs first is non-zero. Together, they support the existence of an entropy crisis at a positive temperature. The importance of a mathematical proof is that it settles the issue once for all. However, another very important consequence of the proof is, as we will see here, that if a phase in some calculation gives rise to an entropy crisis, it means that there must be another (ordered) phase without an entropy crisis. The proof uses general but rigorous thermodynamic and statistical mechanical arguments, valid for classical or quantum systems. We verify our conclusions by two exact calculations, one of which is not a mean-field calculation.

As the issue has remained unresolved for so long most certainly implies that its resolution is not trivial. Thus, it should come as no surprise to the reader that our arguments are somewhat involved, can be divided into several clear parts, and require patience to go through. However, we believe that they are certainly not beyond the reach of a majority of the workers studying glasses. The proof of the validity of the above mechanism follows from the various theorems that we prove here. To guide the reader, we summarize the strategy for the eventual demonstration.

1. We first prove that for $E_D > E_0$, where $E_D$ is the lowest energy for which SMS exists $[S(E) \geq 0]$, the SMS free energy must become equal to the $(T = 0)$-CR free energy $E_0$ at a positive temperature $T_{eq}$. Neither the SMS entropy nor its inverse slope at $E_D$ need vanish for this to hold.

2. We then prove that if the energy of the SMS state is higher than $E_0$, then its temperature must be positive. From this it follows that SMS cannot reach $T = 0$ with an energy $E = E_D > E_0$.

3. We then prove that SMS free energy at $T = 0$ again equals $E_0$ at $T = 0$. Thus, the SMS free energy must have a maximum somewhere in the range $0 < T < T_{eq}$. The entropy at the maximum is zero, identifying the maximum with the Kauzmann point and its temperature with $T_K$. This also identifies the lowest energy $E_D$ with $E_K$, the energy at $T_K$. This energy is greater than $E_0$ because of the non-negative SMS heat capacity.

The existence of the maximum in the SMS free energy thus finally proves the existence of a Kauzmann point.

1.1 Fundamental Postulate

Our general proof assumes the existence of SMS’s, so that thermodynamics can be applied. The need for the assumption is easy to understand. At present, our understanding of whether equilibrium states can be demonstrated to exist mathematically even in simple models is too limited. We should recall that the existence of equilibrium states is taken for granted as a postulate in statistical mechanics and thermodynamics, where it is well known that it is extremely hard to prove their existence. We quote Huang [20]: “Statistical mechanics, however, does not describe how a system approaches equilibrium, nor does it determine whether a system can ever be found to be in equilibrium. It merely states what
the equilibrium situation is for a given system." Ruelle\textsuperscript{21} notes that equilibrium states are defined \textit{operationally} by assuming that the state of an isolated system tends to an equilibrium state as time tends to $+\infty$. Whether a real system actually approaches this state cannot be answered. We make a similar assumption about the existence of SMS within the \textit{restricted} ensemble that will be introduced below. Any analysis of thermal data on glasses and supercooled liquids requires using time-independent thermodynamics, as discussed above. Thus, \textit{hypothesizing} the existence of SMS is perfectly justified by the practice in the field. The existence of supercooled liquids, and glasses in systems with short- or long-range interactions or structural glasses, and their stability over a long periods of time is undeniable. These stable states are a manifestation of SMS in these systems.

Without such an assumption, we cannot justify using conventional (time-independent) thermodynamics to analyze SCL data. The two exact calculations in this work show that the hypothesis is not vacuous. The behavior in real systems is, of course, oblivious to the state of our knowledge and is not controlled by the fact that we can only demonstrate SMS in a few exact calculations.

1.2 Reality Condition and Entropy Crisis

As said above, the entropy $S(T)$, such as the configurational entropy, that we consider in this work represents the natural log of the number of microstates $W(E)$ where $E$ is the average energy at that temperature. For the microstates to exist in Nature, it is evident that $W(E)$ must satisfy the \textit{reality condition} $W(E) \geq 1 \ [S(T) \geq 0]$. However, a state with \textit{negative entropy} can emerge in theoretical calculations or extrapolations. If it happens that the calculations or extrapolations result in a negative $S(T)$ below some positive temperature $T_K$, this should be interpreted as the absence of real microstates available to the system at those temperatures and the system cannot be found in those microstates in Nature. It is this violation of the reality condition $S(T) \geq 0$ that signifies the genuine entropy crisis in Nature.

It should be noted that our criterion for the entropy crisis is much more stringent than the original Kauzmann requirement $S_{ex}(T) < 0$, since it is possible to have $S(T) \geq 0$ even though $S_{ex}(T) < 0$. Thus, our $T_K$ is lower than the corresponding temperature where $S_{ex}(T) = 0$.

There are two \textit{independent} aspects of thermodynamics and statistical mechanics. The first one is the requirement of \textit{stability} according to which thermodynamic quantities like the heat capacity, the compressibility, etc. must never be negative. The other aspect, independent of the stability criteria, is the \textit{reality} condition that ensures that such states occur in Nature\textsuperscript{22}. The reality issue is central in our approach and is discussed further below. We will see below that the mathematical extension of the free energy of the disordered liquid phase below the melting temperature $T_M$ will always satisfy the stability criteria everywhere ($T \geq 0$), but the reality condition is satisfied only above some positive temperature $T_K$. 

5
1.3 Common Folklore

Majority of the calculations displaying stationary metastable states are in spin models, and are carried out at the level of the random-mixing approximation (RMA); the latter is valid in the limit of infinite coordination number $q$ and vanishing interaction strength $J$, keeping $qJ$ is fixed and finite. This approximation is equivalent to solving the models in an infinite-dimensional space. This has given rise to the common folklore that SMS’s occur only in an infinite-dimensional space whose coordination number is also infinite. This is incorrect as we will clearly demonstrate here by an explicit calculation. The calculation is a non-mean-field calculation carried out exactly in a 1-dimensional model and captures SMS. The calculation is presented to overcome this folklore. The model also shows the entropy crisis in SMS. Another alternative way to visualize the RMA is to think of long-range interactions in a finite-dimensional space. Thus, another folklore is that SMS does not exist for short range models. Even frustration is considered in the folklore to be necessary for the glassy behavior. The second example in the work is that of an Ising model with short-range interactions and no frustration. This example establishes not only the existence of SMS in short range models but also that frustration is not necessary for the existence. The model is solved exactly on a Husimi cactus; hence, its thermodynamics is proper.

It is true that the cactus can only be embedded in an infinite dimensional space, but locally it resembles a square lattice which has a finite coordination number. The important point to note is that the interactions are short-ranged. The dimensionality is relevant only if we are interested in critical exponents, which we are not in this work. The finite coordination number of the cactus makes our calculation very different from RMA. Our general proofs are certainly not based on RMA ideas. From all the experience we have accumulated, the cactus provides a much better description of the square lattice model than the conventional mean-field (RMA), as we have shown elsewhere.[23]

2 Formulation

2.1 Canonical Partition Function

The stationary nature of the SMS allows us to investigate it using the partition function (PF) formalism. We consider a system composed of $N$ particles confined in a given volume $V$ and at a given temperature $T$. The thermodynamic limit is obtained by taking the simultaneous limits $N \to \infty$, and $V \to \infty$, such that the volume per particle $v \equiv V/N$ is kept fixed and finite. The internal degrees of freedom of the system contain the configurational (i.e., positional) degrees of freedom and all other degrees of freedom like the translational degrees of freedom coupled to them[24]. The canonical PF determined by these
degrees of freedom is given by

$$Z_N(T) \equiv \widehat{\text{Tr}} \exp(-\beta E),$$

where the trace operation $\widehat{\text{Tr}}$ is over the coupled degrees of freedom and $\beta \equiv 1/T$, $T$ being the system temperature in the units of the Boltzmann constant $k_B$. In the following, we will usually suppress the index $N$ on the PF, unless necessary. The energy of the system $E$ is determined by the coupled degrees of freedom. The PF in (1) is irreducible in that it cannot be written as a product of several non-trivial PF’s corresponding to independent sets of degrees of freedom; see [24]. Some coupling between different degrees of freedom, no matter how weak, is required to achieve equilibrium so that they all share the same common temperature. The weaker the coupling, the longer the time required to come to equilibrium. The temperatures in different PF factors in the product need not be the same as there is no coupling between independent degrees of freedom. Therefore, such a situation does not have to be considered here. We only consider the case of an irreducible PF in this work.

The microstates over which the operation $\widehat{\text{Tr}}$ is carried out in (1) are determined by the coupled degrees of freedom, while the macrostates are determined by the thermodynamic variables $N, V$ and the temperature $T$. Since the degrees of freedom are not part of the macroscopic description, but the average energy defined below is, it is convenient to replace the trace operation in (1) by a trace only over the energy of each microstates. We classify different realizations of the degrees of freedom, i.e. the microstates, according to their energy $E$, so that $W(E)$ is the number of microstates of energy $E$. We can now transform the above PF in (1) into

$$Z(T) \equiv \text{Tr} \ W(E) \exp(-\beta E),$$

where $\text{Tr}$ now stands for the trace operation over the energy (eigenvalues) $E \geq E_0$ up to its maximum. We also introduce the following extensive quantities

$$\Omega(T) \equiv \ln Z, \quad F(T) \equiv -T \ln Z;$$

here, $F(T)$ is the conventional Helmholtz free energy.

Since the sign of the entropy is an important issue in the study of glasses, it is important that the entropy be introduced using the number of microstates $W(E)$, so that $W(E) \geq 1$. This requires some kind of discretization of the degrees of freedom to count the microstates. In the following, we will assume that such a discretization has been carried out so that we always have $W(E) \geq 1$ for states that occur in Nature. This ensures that the corresponding microstate entropy $S(E) \equiv \ln W(E)$ due to the coupled degrees of freedom is non-negative. Despite this, we will see below that negative entropies can be obtained from the free energy associated with the SMS at low temperatures, even though the free energy itself is stable [22]. This will force us to conclude that an ideal glass transition must intervene to avoid the resulting entropy crisis.

The PF in (1) is irreducible. It can happen in some cases that the PF is a product of several non-trivial PF’s corresponding to independent sets of degrees of freedom.
of freedom, each set containing only coupled degrees of freedom; see \[24\]. The application of the reality condition to each set requires that the entropy from each set be non-negative for the system to occur in Nature. The entropy crisis occurs when any of the entropies from the independent sets (each containing coupled degrees of freedom) becomes negative even if the total entropy due to all sets is non-negative.

2.2 Thermodynamic Limit

The thermodynamic limit is obtained by taking \( N \to \infty \), keeping \( v \equiv V/N \) fixed. To make the discussion clear, we will exhibit the subscript \( N \) in various quantities in this subsection. The limit is taken by considering the sequence formed by

\[
\omega_N(T) \equiv (1/N)\Omega_N(T), \quad \text{where} \quad \Omega_N(T) \equiv \ln Z_N(T),
\]

for different values of \( N \) as \( N \to \infty \). The volume may be changed according to \( V = vN \). For proper thermodynamics, the limit of the sequence must exist, which we denote by \( \omega \).

We express the fact that \( V/N \) is fixed by stating that \( V \) is a homogeneous function of order 1 in \( N \). Similarly, the existence of the limit \( \omega \) is expressed by stating that \( \Omega_N(T) \) or \( F_N(T) \equiv -T\ln Z_N \) are homogeneous functions of order 1 in \( N \). One can also say that the temperature \( T \) is a homogeneous function of order 0 in \( N \). The average energy \( E_N(T) \) and the entropy \( S_N(T) \) are homogeneous functions of order 1 in \( N \). For any quantity \( Q_N \), which is a homogeneous function of order 1 in \( N \), the ratio \( Q_N/N \) is a homogeneous function of order 0 in \( N \) and must possess a limit \( q \) as \( N \to \infty \). We express this fact in the following as

\[
Q_N/N \sim q,
\]

whose significance is as follows: for finite \( N \), the meaning of (4) is that the right side may differ from \( q \), but the difference vanishes as \( N \to \infty \).

Remark 1: In the following, whenever we compare different extensive quantities \( Q_i \) or different PF’s \( Z_i \), it is implicit that we are comparing the ratios \( Q_i/N \) or \( \ln Z_i/N \), respectively.

2.3 Continuous Energy and Entropy Functions for Finite \( N \)

The average energy and entropy in the canonical ensemble are continuous functions of \( T \) and are given by

\[
\begin{align*}
\overline{E}(T) & \equiv -\langle \partial \Omega / \partial \beta \rangle, \\
\overline{S}(T) & \equiv -\langle \partial F / \partial T \rangle,
\end{align*}
\]

respectively; we have suppressed the subscript \( N \) for simplicity. They should not be confused with the microstate energy \( E \) and entropy \( S(E) \). To see this
clearly, we rewrite (5b) as $\mathcal{S} = \ln Z + E/T$, and exponentiate it. We can use the explicit $T$-dependence of $\mathcal{E}(T)$ to express $\mathcal{S}(T)$ as an explicit function $S(\mathcal{E})$ of $\mathcal{E} \equiv \mathcal{E}(T)$. Introducing $W(E) \equiv \exp[S(E)]$, we have

$$W(\mathcal{E}) = \text{Tr} W(E) e^{-\beta(E-\mathcal{E})} = W(E_m) e^{-\beta(E_m-\mathcal{E})} + \text{Tr}' W(E) e^{-\beta(E-\mathcal{E})},$$

(6)

where the prime on the trace indicates that some microstate energy $E = E_m$ is not allowed in the trace. For a finite system ($N < \infty$), the allowed microstate energy $E$, and the microstate entropy $S(E) \equiv \ln W(E)$ are discrete, while the average energy $\overline{E}$ and the average entropy $\overline{S}$ are continuous functions. Let us consider the case when the average energy is exactly equal to the microstate energy $E_m$. From (6), we observe that

$$W(\mathcal{E}) \geq W(E_m).$$

(7)

The left side in (7) represents the value of the continuous function $W(\mathcal{E} = E_m)$, while the right side is the discrete quantity $W(E_m)$ for the finite system. The difference between them is due to the last term in (6), which is non-negative, which vanishes as $N \to \infty$. For finite $N$, the microstate entropy $S(E)$ represent isolated points, which get closer and closer to the continuous function $S(\mathcal{E})$ as $N$ increases, and cover it entirely as $N \to \infty$. Similarly, $\overline{E}$ represents a continuous variable, and contains in its range isolated values given by the microstate energies; the latter cover the entire range of $\mathcal{E}$ as $N \to \infty$.

The continuous function $S(\mathcal{E})$ is amenable to differentiation, which is not possible with the discrete set of points $S(E)$, and contains all the useful physical information. Because of this, there is no harm in expressing $S(\mathcal{E})$ simply by $S(E)$; the latter now represents a continuous function. Similarly, there is no harm in expressing the continuous variable $\mathcal{E}$ by $E$. This is a common practice in the literature. Whenever we need to make a distinction between the discrete values and the continuous functions, we will speak of the values related to microstates in the former case, and of average values in the latter case. Similarly, we use $S(T)$ to express the entropy $\overline{S}(T) \equiv S(\mathcal{E})$ as a function of $T$, where $T$ is the temperature at which the average energy from (5a) is $\mathcal{E}$. The use of the continuous functions enables us to consider the entropy for any value of the energy, whether it represents the energy of a microstate or not. The continuous entropy function satisfies the following relation:

$$\frac{\partial S}{\partial E} \equiv \frac{(\partial S/\partial T) / (\partial E/\partial T)}{1/T} \equiv 1/T.$$  

(8)

Let us first illustrate the above points by a simple example. Consider two ferromagnetically interacting (interaction strength $-J$) Ising spins in the absence of any external magnetic field. There are four microstates, two with $E = -J$ (the lowest possible energy), and two with $E = J$ (the highest possible energy). Thus, there are only two microstate energies, each having the microstate entropy $\ln 2$. On the other hand, the average energy and entropy are continuous functions of $T$. To see this, we calculate the canonical PF, which is $Z \equiv 4 \cosh K$,
where $K = J/T$. A simple calculation for the average energy and entropy yields

$$E = -J \tanh K, \quad S = \ln(4 \cosh K) - K \tanh K.$$  

We observe that the energy ranges continuously between $-J$ and 0, and the entropy ranges continuously between $\ln 2$ and $\ln 4$ for $T \geq 0$. (The energy range between 0 and $J$ corresponds to negative temperatures that we do not consider here.) The average energy and entropy are $(-J)$ and $\ln 2$, respectively, as $T \to 0$, and 0 and $\ln 4$, respectively, as $T \to \infty$, as expected. The average energy, and entropy fill continuously the microstate energy and entropy gap, respectively. The important point is that the lowest energy corresponds to the absolute zero of the temperature.

We now prove that the entropy slope relation in (8) is valid for any $N$, finite or not. We consider the PF in (2) for finite $N$. We start with the continuous entropy and energy functions related by $TS = E - F$. Differentiating on both sides with respect to $T$, we find

$$S + T(\partial S/\partial T) = (\partial E/\partial T) + \ln Z + T(\partial Z/\partial T)/Z.$$  

Recognizing that

$$(\partial Z/\partial T) = (1/T^2)\text{Tr} \ W(E) \exp(-\beta E),$$  

we find that the above equation reduces to

$$T(\partial S/\partial T) = (\partial E/\partial T),$$  

which proves (8) for finite $N$. The limit $N \to \infty$ is considered by dividing both sides of $TS = E - F$ by $N$, and carrying out the same steps.

We now argue that if we replace $W(E)$ by $W(E)$ in (2) to define a new PF

$$\overline{Z}(T) = T \text{r} W(E) e^{-\beta E},$$  

in which the trace is still over the microstate energies, then using $S = \ln Z + E/T$, and $W(E) \equiv \exp(S)$, we find that

$$\overline{Z}(T) \equiv Z(T) \text{r} 1 \sim Z(T),$$  

since $\text{r} 1$ is the number of distinct microstate energies and satisfies $\ln(\text{r} 1)/N \sim 0$. Consequently, $\ln \overline{Z}(T)/N$ and $\ln Z(T)/N$ are the same in the sense of the above Remark 1. In the following, we will consider both versions of the PF for macroscopically large but finite systems, as they are identical in all thermodynamic consequences. Indeed, it is a common practice in the literature not to make any distinction at all. Because of this, we will denote both of them by $Z(T)$; we will indicate the difference whenever needed.

Remark 2: It should be noted that the association of the slope in (8) with the temperature $T$ requires fixing the temperature of the system. The temperature is fixed from outside, such as by using a heat bath, and must be independent of the size $N$ of the system, even though both $S$ and $E$ depend on $N$ in accordance with (4). In this sense, the significance of $T \equiv 1/(\partial S/\partial E)$ is that for any $N$, there exists an $E$ so that (8) is always satisfied.
2.4 Configurational PF

In classical statistical mechanics (CSM), the positional degrees of freedom are independent of the translational (i.e., momentum) degrees of freedom when the collisions are neglected. In this case, the PF can be written as a product of two PF’s. One of them is $Z_{KE}(T_{KE})$ determined by the momentum degrees of freedom; here $T_{KE}$ is the temperature associated with these degrees of freedom and the energy associated with these degrees of freedom is the kinetic energy of the system. (It should be noted that the momentum degrees of freedom are also independent of each other so each momentum degree of freedom can have its own temperature. We will not worry about this complication.) The other factor is the PF $Z(T)$, known conventionally as the configurational PF at a temperature $T$. It is determined only by the positional degrees of freedom for which the energy is the potential energy in the system. The collisions between particles are neglected so the two sets of the degrees of freedom have no mechanism to come to equilibrium. Hence, there is no way for the two temperatures to be the same. Usually, it is assumed that there exists a weak coupling between the two degrees of freedom, which is sufficient to bring about eventual equilibrium between them. Thus, to a good approximation, the above factorization is taken to be valid in real systems. The important observation is that the value of $Z_{KE}$ is independent of the value of the configurational PF $Z(T)$ at this level of the approximation. Consequently, the total entropy $S_{tot}(T)$ due to both energies is additive: $S_{tot}(T) = S(T) + S_{KE}(T)$, where $S_{KE}(T)$ is the entropy due to the kinetic energy and is independent of the configurations of the system. Furthermore, $S_{KE}(T)$ is the same for all kinds of systems. Thus, $Z_{KE}(T)$ is not of any interest when studying any particular system. Because of this, there is no harm in restricting our attention to the studying the configurational PF $Z(T)$. In this case, the PF in (2) represents the configurational PF $Z(T)$ as defined conventionally in CSM so that $S(T)$ will represent the conventional configurational entropy in CSM. The entropy crisis occurs when $S(T)$ becomes negative, even if $S_{tot}(T)$ is non-negative.

2.5 Quantum PF

In quantum statistical mechanics (QSM), the kinetic energy is an operator and cannot be separated out from the total PF[24]. The role of the configurational PF is now played by the total PF. The energy $E$ in (2) now represents the eigenvalues of the total (potential+ kinetic) energy, and $S(T)$ derived from (2) now represents the total entropy, which cannot be broken into additive terms as was the case in CSM above. Thus, one cannot define the classical configurational entropy in QSM. We can think of $S(T)$ derived from (2) as the quantum analog of this classical concept.

The irreducible PF $Z(T)$ in (2) is the general form of the PF valid in both CSM and QSM, with $S(T) = S(E)$ equal to the conventional configurational entropy in CSM, and the total entropy in QSM. From now onward, we will no longer explicitly distinguish between the classical and quantum PF’s. Our
discussion is going to be valid for both cases.

2.6 Conditions for Equilibrium and Negative Entropy

For the lowest allowed energy $E_0$, we must surely have $W(E_0) \neq 0$. Assuming $TS(T) \to 0$ as $T \to 0$, we recognize that $E_0$ represents not only the Helmholtz free energy but also the energy of the perfect CR at $T = 0$. (We assume that CR has the lowest free energy at low temperatures.) Since $W(E)$ is non-negative, $Z$ is a sum of positive terms. Because of this, the probability of every microstate is strictly non-negative. As a consequence, the following two principles are always satisfied.

1. Maximization Principle. The PF $Z$ must be maximized in the thermodynamic limit $N \to \infty$, keeping $V/N$ fixed. The maximum value of $Z(T)$ corresponds to picking out the maximum term $e^{S - \beta E}$ in (2). This maximum term corresponds to $E = \overline{E}$, defined above.

2. Stability Principle. The heat capacity, which is given by the fluctuations in the energy is non-negative. This remains true even in the thermodynamic limit.

It should be stressed that the non-negativity of the heat capacity and the maximization principle only require the positivity of $W(E)$. Thus, both principles remain valid even if the entropy becomes negative. Stability and reality are two independent aspects of our formalism. This observation is going to be useful when we discuss the metastable states below.

3 Stationary Metastable States and Restricted Ensemble

3.1 Infinite System

Conventional statistical mechanics describes equilibrium states, which satisfy the above two principles of reality and global maximization. For this, it is necessary that we have $N \to \infty$. The existence of a melting transition, which also requires $N \to \infty$, at $T_M$ means that the disordered equilibrium liquid (EL) phase above $T_M$ and the ordered CR below $T_M$ correspond to different values of the order parameter $\rho$, which is traditionally used to distinguish various phases of the system, with $\rho = 0$ representing the disordered phase and $\rho \neq 0$ the ordered phase CR. (One of our examples below will show explicitly how the microstates can be divided into the two disjoint classes.) We assume here for simplicity that there is only one kind of ordered phase. The extension to the case of many disjoint ordered states with different non-zero values of $\rho$ is easy to incorporate in the approach. This distinction in the order parameter is easily made in the case $N \to \infty$, by denoting the free energy per particle ($N \to \infty$) above $T_M$ by $f_{\text{dis}}(T)$, and below $T_M$ by $f_{\text{ord}}(T)$, from which we can calculate the entropies, and energies per particle

\[ s_\alpha(T) \equiv -(\partial f_\alpha/\partial T), \quad e_\alpha(T) \equiv -(\partial \beta f_\alpha/\partial \beta), \quad \alpha = \text{dis, ord}, \]  

\[ \text{(11)} \]
respectively, corresponding to the two states. Due to the limit $N \to \infty$, the per particle microstate entropies and continuous entropy functions are equal at the same $e$. Thus, we can think of the continuous entropy and energy functions $s_{\alpha}(E)$, and $e_{\alpha}(T)$ for the two states.

The global maximization, which operates when $N \to \infty$, is required to argue that $f_{\text{ord}}(T)$ is the equilibrium state free energy (for CR) below $T_M$, and $f_{\text{dis}}(T)$ the equilibrium state free energy (for EL) above $T_M$:

\begin{align}
  f(T) &= f_{\text{ord}}(T) \quad T < T_M, \quad (12a) \\
  f(T) &= f_{\text{dis}}(T) \quad T > T_M. \quad (12b)
\end{align}

Thus, incorporating the global maximization principle will not allow us to describe SCL. The singularity in the equilibrium free energy per particle $f(T)$ at $T_M$ in (12a, 12b), which forces it to switch from $f_{\text{dis}}(T)$ to $f_{\text{ord}}(T)$ at $T_M$, is a hallmark of the a phase transition. This singularity in $f(T)$ does not necessarily imply a singularity in either of its two pieces $f_{\text{dis}}(T)$ and $f_{\text{ord}}(T)$. Both of them can exist on either side of $T_M$. This possible extension is not a consequence of a mean-field approximation, as our first example will demonstrate. A consequence of this is that the functions $s_{\alpha}(T)$, and $e_{\alpha}(T)$ also exist on either side of $T_M$. In the following, we are only interested in the case in which $s_{\text{dis}}(T)$, and $e_{\text{dis}}(T)$ exist all the way down to $T = 0$.

A prescription to describe metastability using the PF formalism can now be formulated.

**Metastability Prescription** We abandon the global maximization principle, and use $f_{\text{dis}}(T)$ to give the free energy of the metastable disordered phase (supercooled liquid) below $T_M$ and $f_{\text{ord}}(T)$ to give the metastable (superheated crystal) state free energy above $T_M$. Similarly, $s_{\text{dis}}(T)$, $e_{\text{dis}}(T)$ and $s_{\text{ord}}(T)$, $e_{\text{dis}}(T)$ give the entropy and energy per particle for the supercooled liquid and superheated crystal, respectively.

However, in this work, we are only interested in the supercooled liquid.

### 3.2 Finite System

The study of an infinite system allows us to identify ordered ($\rho \neq 0$) and disordered ($\rho = 0$) microstates and gives their entropy and energy per particle $s_{\alpha}(T)$, and $e_{\alpha}(T)$, respectively. The identification is useful to classify each microstate as ordered ($\rho \neq 0$) or disordered ($\rho = 0$). This does not imply that it is feasible to count these microstates for an infinite system in which there are infinite microstates. For a complete analysis, we need to be able to count in principle the microstates and classify them. For this, we need to consider the case of finite but large $N$. In this case, the continuous entropy and energy functions for the entire system are $S_{\alpha}(T) \sim N s_{\alpha}(T)$, and $E_{\alpha}(T) \sim N e_{\alpha}(T)$. We also consider the continuous functions $S_{\alpha}(E)$, and $W_{\alpha}(E) \equiv \exp[S_{\alpha}(E)]$ which, as we show later, exist for all energies $E \geq E_0$. As said earlier, the continuous function $W_{\alpha}(E)$ for microstate energy $E$ is close to the number of ordered and disordered microstates of microstate energy $E$; see [7].
The total number of microstates $W(E)$ with microstate energy $E$ can be written as a sum of the number of microstates $W_{\text{ord}}(E)$ consistent with $\rho = 0$, and the number of microstates $W_{\text{dis}}(E)$ consistent with $\rho \neq 0$, so that

$$W(E) \equiv W_{\text{ord}}(E) + W_{\text{dis}}(E).$$

(Presence of other configurations will not affect our argument.) While $W_{\text{ord}}(E)$ certainly exists for microstate energies starting from $E = E_0$, there is no guarantee that $W_{\text{dis}}(E)$ also exists near $E = E_0$. Most probably, microstate $W_{\text{dis}}(E) \geq 1$ does not continue all the way down to $E = E_0$. If it did, the energy of the disordered phase at absolute zero would be $E_0$, the same as that of CR. This would most certainly imply that they would coexist at $T = 0$, each having the same volume; recall that we are considering a fixed volume ensemble. While there is no thermodynamic argument against it, it does not seem to be the case normally. Usually, the most stable state at $T = 0$ is that of a crystal. Moreover, it is an experimental fact\(^{[1]}\) that all glasses have much higher energies or enthalpies compared to their crystalline forms at low temperatures; see (Expt2) above. Anticipating that the ideal glass, which is the stationary limit of all observed glasses, should have its energy higher than $E_0$, we conclude that the lowest possible energy $E_K$ for the disordered state is strictly larger than $E_0$. In other words, the microstate number $W_{\text{dis}}(E)$ has the following property:

$$W_{\text{dis}}(E) = 0 \text{ for } E < E_K, \quad \text{(14a)}$$

$$W_{\text{dis}}(E) \geq 1 \text{ for } E \geq E_K. \quad \text{(14b)}$$

On the other hand, we are only interested in considering the case when $S_{\text{dis}}(T)$ exists for all $T \geq 0$. Thus, $S_{\text{dis}}(T)$ exists for all $T \geq 0$. We will show later that the temperature $T = T_K = 1/(\partial S_{\text{dis}}/\partial E)$ at $E_K > E_0$ corresponding to the disordered phase is strictly positive. Thus, $S_{\text{dis}}(T)$ [or $S_{\text{dis}}(E)$] must be negative below $T = T_K$ [or $E = E_K$]. We will, in fact, see that $S_{\text{dis}}(E)$ continues all the way down to $E_0$.

### 3.3 Restricted Ensemble

We continue with finite but large $N$. Using the continuous forms of $W_{\text{ord}}(E)$ and $W_{\text{dis}}(E)$, we introduce the following restricted ensemble approach to describe metastable states\(^{[2]}\). We follow (9) and we introduce two new PF’s using (2) by replacing continuous $W(E)$ by continuous $W_{\text{ord}}(E)$ and $W_{\text{dis}}(E)$, respectively:

$$Z_\alpha(T) \equiv TrW_\alpha(E) \exp(-\beta E), \quad \alpha = \text{dis, ord},$$

and the corresponding free energies

$$F_\alpha(T) \equiv -T \ln Z_\alpha(T), \quad \alpha = \text{dis, ord}. \quad \text{(16)}$$

As $N \to \infty$, $F_\alpha(T)/N \to f_\alpha(T)$. 

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Above the melting temperature $T_M$, $Z_{\text{dis}} > Z_{\text{ord}}$, and below $T_M$, $Z_{\text{dis}} < Z_{\text{ord}}$. The use of the maximization principle describes CR and EL collectively for thermodynamically large $N$:

$$Z_{\text{dis}}(T) > Z_{\text{ord}}(T), \quad T > T_M; \quad (17a)$$
$$Z_{\text{ord}}(T) > Z_{\text{dis}}(T), \quad T < T_M; \quad (17b)$$

so that

$$F_{\text{ord}}(T) > F_{\text{dis}}(T), \quad T > T_M; \quad (17c)$$
$$F_{\text{dis}}(T) > F_{\text{ord}}(T), \quad T < T_M. \quad (17d)$$

For finite $N$, there cannot be any singularity at $T_M$, so that $F_{\text{dis}}(T)$ or $F_{\text{ord}}(T)$ has no singularity of its own at $T_M$, i.e., they exist on both sides of $T_M$. We now describe SMS by the PF $Z_{\text{dis}}(T)$ below $T_M$. The continuation necessarily yields $\rho = 0$ also for SCL.

The entropy functions $S_{\alpha}(E)$ are shown in Fig. 1: OHAB represents $S_{\text{ord}}(E)$, and KCO AD represents $S_{\text{dis}}(E)$. The entropy as a function of $E$ must be thought of as the entropy in the microcanonical ensemble[25], which must be maximum for the equilibrium state. Since a SMS is not an equilibrium state in the unrestricted ensemble, its entropy at some $E$ cannot exceed the entropy of the corresponding equilibrium state at the same $E$. A consequence of this entropy condition is that the free energy $F_{\text{dis}}(T)$ of SMS cannot be lower than the free energy $F_{\text{ord}}(T)$ of CR at the same temperature $T$. This explains the form of the entropy and free energy in Fig. 1. The two free energies are shown in the inset by OAB representing $F_{\text{ord}}(T)$, and OKCO’D representing $F_{\text{dis}}(T)$. The form of the entropy and free energy is also supported by all known observations[1, 2], exact[7, 8, 12] and numerical[6] calculations, and from the arguments and the calculations presented below. We note that

$$S_{\text{ord}}(E) < S_{\text{dis}}(E), \quad E > E_M; \quad (18a)$$
$$S_{\text{dis}}(E) < S_{\text{ord}}(E), \quad E < E_M; \quad (18b)$$

where $E_M$ is the energy at A where $S_{\text{ord}}(E) = S_{\text{dis}}(E)$; see Fig. 1. The SMS corresponding to the stationary SCL is defined by the branch KCAH’. Similarly, superheated CR is defined by the branch HAB. We note that the entropy $S_{\text{dis}}$ of the metastable branch goes to zero at $T_K > 0$. This behavior is supported by our rigorous proof and by two exact calculations in the paper. However, we will allow the possibility in our discussion below that the lowest energy for $S_{\text{dis}}$ is $E_D$, and that $S_{\text{dis}}(E_D) > 0$. We also show the entropy function for a non-stationary metastable state by GF in Fig. 1, assuming that crystallization is forbidden. We do not consider the non-stationary state GF anymore.

### 3.4 A Useful Theorem

We now prove an extremely useful theorem.
Theorem 1
Since $E_K > E_0$, the free energy $F_{\text{dis}}(T_{eq})$ at $O'$ equals the free energy $F_{\text{ord}}(T = 0) = E_0$ at $O$, where $T_{eq}$ is the inverse of the slope of the line $OO'$ touching the entropy function $S_{\text{dis}}(E)$, which vanishes at $E = E_K$; see point $O'$ in the inset in Fig. 1.

The proof is very simple. The slope $1/T_{eq}$ of $OO'$ is given by

$$1/T_{eq} = S_{\text{dis}}(E_{O'})/(E_{O'} - E_0),$$

where $E_{O'}$ is the energy at $O'$. Thus,

$$E_0 = E_{O'} - T_{eq}S_{\text{dis}}(E_{O'}).$$

Since the slope of $S_{\text{dis}}(E_{O'})$ at $E_{O'}$ is $1/T_{eq}$, the right side represents the free energy $F_{\text{dis}}(T_{eq})$ of the SMS at $O$. The left side represents the free energy of CR at $T = 0$. This proves the theorem.

It should be stressed that the proof does not use the vanishing of $S_{\text{dis}}(E_K)$. Thus, the equality $F_{\text{dis}}(T_{eq}) = E_0$ is also valid if $S_{\text{dis}}(E_D) > 0$. The proof also does not depend on the entropy slope at $E_D$ or $E_K$. The proof only requires that this slope be larger than or equal to $1/T_{eq}$.

We now consider the behavior of $Z_{\text{dis}}(T)$. Since the continuous entropy $S_{\text{dis}}(E)$ is real, we have $W_{\text{dis}}(E) > 0$. Thus, we observe that $Z_{\text{dis}}(T)$ is a sum of positive terms. Because of this, $Z_{\text{dis}}(T)$ also satisfies the maximization and stability principles, just as $Z(T)$ does. The only difference is that they are only valid in the restricted ensemble of the disordered microstates corresponding to $\rho = 0$.

The reality condition cannot be violated, even for a SMS if it is observable. Therefore, its violation ($S_{\text{dis}}(T) < 0$ for $T < T_K > 0$) implies that SMS cannot exist in Nature when the violation occurs, in which case the SMS associated with the SCL must be replaced by a new state, commonly known as the ideal glass state below $T_K$, whose energy at $T \leq T_K > 0$ is $E_K > E_0[1,2]$. The transition between the two states is called the ideal glass transition.

4 Finite Entropy Slope of the Disordered Phase

Theorem 2
The slope of the entropy function $S_{\text{dis}}$ at $E/E_0 > 1$ must be finite.

We again consider finite and infinite $N$ separately.

4.1 Finite $N$

We consider the average entropy functions $S_\alpha(E)$ for fixed $V,N$; see Fig. 1, where they are shown schematically as functions of $E$. According to $\S$,

$$\frac{\partial S}{\partial E} \equiv 1/T, \quad \frac{\partial S_\alpha}{\partial E} \equiv 1/T_\alpha, \quad \text{(19)}$$

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where $1/T$, $1/T_\alpha$ represent the inverse temperatures corresponding to $S$, $S_\alpha$, respectively. By introducing the entropy and energy densities

$$s_N \equiv S/N, \quad s_\alpha,N \equiv S_\alpha/N, \quad e_N \equiv E/N,$$

we can rewrite (19) that will be useful in taking the thermodynamic limit below.

For finite $N$, $s_N$, $s_\alpha,N$, and $e_N$ are homogeneous functions of order 0; see (4).

The behavior of the slope in (19) for the disordered phase is critical in understanding what happens at $K$, the Kauzmann point (where $S_{\text{dis}} = 0$). There are two distinct possibilities. The slope at $K$ is either finite, as shown explicitly in Fig. 1 and consistent with our rigorous analysis, or infinite. The former corresponds to a positive $T_K$, while the latter corresponds to an absence of a Kauzmann paradox ($T_K = 0$). Almost all explicit calculations show the former as the usual behavior, two of which are presented below.

To proceed further, we consider (13) for any microstate energy. From what has been said earlier about the continuous function $S(E)$, we extend (13) to any allowed continuous energy so that it can be differentiated. Taking the derivative with respect to $E$ on both sides, we find that

$$W(\partial S/\partial E) \equiv W_{\text{ord}}(\partial S_{\text{ord}}/\partial E) + X_{\text{dis}}(\partial S_{\text{dis}}/\partial E).$$

We introduce the ratios $X_\alpha \equiv W_\alpha/W$ ($0 \leq X_\alpha \leq 1$) and rewrite the above equation as

$$1/T = X_{\text{ord}}/T_{\text{ord}} + X_{\text{dis}}/T_{\text{dis}}.$$  \hspace{1cm} (21)

For $T > T_M$, $X_{\text{ord}} \approx \exp(S_{\text{ord}} - S_{\text{dis}}) \ll 1$, while $X_{\text{dis}} \approx 1$. For $T < T_M$, $X_{\text{dis}} \approx \exp(S_{\text{dis}} - S_{\text{ord}}) \ll 1$, while $X_{\text{ord}} \approx 1$. Let us apply this relation to the crystal at a temperature $T_M > T > 0$ at which the average CR energy is $E > E_0$. It is clear that for any finite $N$, no matter how large, $X_{\text{dis}} > 0$. At the same time, the temperature $T$ must be close to $T_{\text{ord}}$ of the CR, which is strictly positive, since $E > E_0$. This is possible only if

$$T_{\text{dis}} > 0 \quad \text{for} \quad E/E_0 > 1.$$  \hspace{1cm} (22)

Thus, as long as $E > E_0$, the temperature of the disordered phase at $E$ must be positive. This proves the theorem for finite $N$.

4.2 Infinite $N$

Let us now take the limit $N \to \infty$. We only consider the interesting range $T_M > T > 0$. The values of $E$ and $S$ keep changing with $N$ for a given $T$. Thus, it is convenient to consider the sequences $\{e_N\}$ and $\{s_{\alpha,N}\}$ for different $N$, so that $(\partial s_{\alpha,N}/\partial e_N) = 1/T_{\text{dis}} > 0$. We now consider (21) for larger and larger $N$, such that $T_{\text{dis}} > 0$ is kept fixed. From what was said earlier, it is clear that $X_{\text{dis}} \to 0$ from above, so that $T \to T_{\text{ord}}$ from below. But at every step of the limit $N \to \infty$, (22) remains valid. Thus, $T_{\text{dis}} > 0$ for $E/E_0 > 1$ even when $N \to \infty$. 

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The above proof of (22) neither requires nor shows that the entropy $S_{\text{dis}}(E) = 0$ for $E > E_0$. It also does not depend on the sign of $S_{\text{dis}}(E)$ as long as it remains differentiable. It only requires $W_\alpha$ to be non-negative for $T_\alpha$ to be real. Thus, it does not directly prove the existence of a Kauzmann point below which the entropy crisis would occur ($W_{\text{dis}} < 1$). For this, we need to show that the entropy of the disordered phase becomes zero at some $E_K > E_0$. Then the above theorem proves that this occurs at a positive temperature. Furthermore, it shows that the disordered phase can reach the absolute zero only if $E = E_0$.

The proof that an entropy crisis does occur in general at a positive temperature is given in the following section.

5 Free Energy at $T = 0$

We now prove the following theorem.

**Theorem 3** The free energy $F_\alpha$ of all stable phases, mathematically continued or not, are equal in that $F_\alpha/E_0 \to 1$, provided $T s_\alpha \to 0$ as $T \to 0$. Their entropies $s_\alpha$, however, may be different.

The proof will require considering finite $N$ and then taking the thermodynamic limit later just as above.

### 5.1 Finite $N$

Consider finite $N$. From (14a), we conclude that microscopic entropy $S_{\text{dis}}(E)$ does not exist (as a bounded quantity) for $E < E_K$. On the other hand, it must be close to the continuous function $S_{\text{dis}}(E)$ exists only for $E \geq E_K$, and vanishes at $E_K$, as shown in Fig. 1. This is consistent with (14b). From Theorem 2, we conclude that the temperature $T_K$ corresponding to $S_{\text{dis}}(E)$ at $E_K$ is positive.

Moreover, since $N$ is finite, $S_{\text{dis}}(E)$ is not singular at $E_K$. (Recall again that the singularity can only appear in the limit $N \to \infty$.) Then, it can be continued mathematically as a real function below $E_K$ all the way down to $E_0$. But the continuation of $S_{\text{dis}}(E)$ for $E < E_K$, which must necessarily lead to negative $S_{\text{dis}}(E)$ there, is certainly not close to the microscopic entropy $S_{\text{dis}}(E)$ ($= -\infty$). Thus, the mathematical continuation of $S_{\text{dis}}(E)$ below $E_K$ will most certainly not represent the physics correctly. This is not surprising in view of the fact that it violates the reality condition. Despite this, the continuous entropy is still useful in the investigation, and we will allow it to become negative below $E_K$, as it allows us to draw a very important conclusion, as we demonstrate below. Corresponding, we will allow $W_{\text{dis}}(E) < 1$ under continuation.

Due to the mathematical continuation of $W_{\text{dis}}(E)$, both PF’s $Z_{\alpha}(T)$, $\alpha = \text{dis, ord}$, contain all energies from $E_0$ upwards, so that both can be investigated in a unified fashion. As long as $W_\alpha(E) \geq 0$, $Z_{\alpha}(T)$ is a sum of positive terms, so that $\Omega_\alpha(T) \equiv \ln Z_{\alpha}(T)$ satisfies stability principle. For example, the free energy
$F_{\text{dis}}(T)$ is a concave function (a function which always lies above the line joining any two points on it) of $T$, as shown in the inset in Fig. 1 by OKCD. We take out the term corresponding to $E = E_0$ from the trace operation, and express

$$Z_\alpha(T) = W_\alpha(E_0) e^{-\beta E_0} [1 + \tilde{Z}_\alpha'(T)],$$

(23)

where we have introduced a new quantity

$$\tilde{Z}_\alpha'(T) \equiv T r'[W_\alpha(E)/W_\alpha(E_0)] e^{-\beta (E - E_0)},$$

(24)

in which the trace operation $T r'$ is restricted to all $E > E_0$. It is assumed that $W_\alpha(E_0) > 0$. Since $E - E_0 > 0$, we note that $e^{-\beta (E - E_0)} \to 0$ as $T \to 0$. For finite $N$, $W_\alpha(E)$ is a bounded quantity, and so is the ratio $W_\alpha(E)/W_\alpha(E_0)$. Hence, the product under the trace in (24) vanishes, and so does $Z_\alpha(T)$ as $T \to 0$. We finally have

$$Z_\alpha(T) \to W_\alpha(E_0) e^{-\beta E_0} \text{ as } T \to 0.$$

We thus find that $F_\alpha(T) \to E_0 - T S_\alpha(E_0)$ as $T \to 0$. From the boundedness of $W_\alpha(E_0) > 0$, we also conclude that $T S_\alpha \to 0$ as $T \to 0$; hence,

$$F_\alpha/E_0 \to 1 \quad \text{as } T \to 0$$

(25)

for CR and SMS.

### 5.2 Infinite $N$

We recognize that both $F_\alpha$ and $E_0$ are homogeneous functions of order 1 in $N$. Thus, their ratio $F_\alpha/E_0$ is a homogeneous functions of order 0 in $N$. Consequently, we can take the thermodynamic limit $N \to \infty$ by exploiting (24) without altering the conclusion $F_\alpha/E_0 \to 1$ as $T \to 0$. Thus, we finally conclude that both CR and SMS have identical energies $E_0$ at absolute zero in the sense that the energy per particle is the same in both states. However, while the entropy of CR vanishes, that of the mathematically continued SMS has a negative entropy at $T = 0$. Thus, they are not identical.

**Corollary 4** The free energy $F_{\text{dis}}(T)$, mathematically continued to $T = 0$, must have a maximum at the Kauzmann point $T = T_K$ at which the entropy vanishes.

From Theorem 1, we know that $F_{\text{dis}}(T) = E_0$ at $T = T_{eq} > 0$; see point O' in Fig. 1. From Theorem 3, we also know that $F_{\text{dis}}(T) = E_0$ at $T = 0$. Because of the non-negative heat capacity $[\partial^2 F_{\text{dis}}/\partial T^2 < 0]$, $F_{\text{dis}}(T)$ is a concave function of $T$. Thus, the mathematically continued $F_{\text{dis}}(T)$ must have a maximum between the range $(0, T_{eq})$ as shown in the inset in Fig. 1. This maximum at $T = T_K$ corresponds to the Kauzmann point at which the entropy vanishes.

Note from Fig. 1, see OO', that the equality $F_{\text{dis}}(T) = E_0$ at $T = T_{eq}$ is independent of the way $S_{\text{dis}}$ approaches zero at $E_K$. In particular, it does not depend on whether there is a singularity in $S_{\text{dis}}$ at $E_K$, or whether $S_{\text{dis}}$ approaches $E_K$ with a finite slope. Thus, the existence of a maximum in $F_{\text{dis}}(T)$
at $T = T_K$ is not a consequence of Theorem 1 alone. We need the additional result of Theorem 3.

The SMS we have defined mathematically between $T = 0$ and $T = T_K$ cannot represent a state of any real system because of the negative entropy, and must be replaced by the ideal glass, which is a state that has zero entropy and a constant energy $E_K$ and represents the stationary limit of the glassy states observed in experiments. Consequently, this stationary limit of the glassy state is different not only from the CR, but also from the SMS near absolute zero. As SMS is cooled to $T = T_K$, where it has the energy $E_K > E_0$, it turns into the ideal glass.

This completes the proof of the generality of our proposed mechanism. In CSM, $S$ represents the classical configurational entropy, and in QSM, it represents the total entropy $^{24}$. Thus, $T_K$ corresponds to vanishing of different entropies in the two cases. Any attempt to estimate the classical configurational entropy in QSM, where it has no meaning, will require some sort of approximation, which we do not consider here.

The discussion also establishes that the Kauzmann point in the disordered phase exists only when there exists another equilibrium state; otherwise, there will be no partitioning and, therefore, there will be no Kauzmann point. This is most clearly seen in the first example given below.

6 Exact Model Calculations

We consider two CSM models in which we obtain positive Kauzmann temperature. The calculations are carried out exactly. The first example also shows how $\rho$ is used to distinguish different phases, while the second example shows that frustration is not necessary for the glass transition.

6.1 One-dimensional Axis Spin Model

We now consider a one-dimensional axis spin model, which contains $m$-component spins $\mathbf{S}_i$ located at site $i$ of the one-dimensional lattice of $N$ sites, with periodic boundary condition ($\mathbf{S}_{N+1} = \mathbf{S}_1$). Each spin can point along or against the axes (labeled $1 \leq k \leq m$) of an $m$-dimensional spin space and is of length $\sqrt{m}: \mathbf{S} = (0, 0, \ldots, \pm \sqrt{m}, 0, \ldots)$. The spins interact via a ferromagnetic nearest-neighbor interaction energy $(-J)$, with $K \equiv J/T > 0$. The energy of the interaction is given by

$$E = -J \sum_{i=1 \ldots N} \mathbf{S}_i \cdot \mathbf{S}_{i+1}.$$ 

The PF is given by

$$Z_N(K, m) \equiv \left( \frac{1}{2m} \right)^N \sum \exp(-\beta E) = \left( \frac{1}{2m} \right)^N \text{Tr} \hat{T}^N,$$

(26)
where the first sum is over the \((2m)^N\) spin states of the \(N\) spins and \(\hat{T} \equiv \exp(KS \cdot S')\) is the transfer matrix between two neighboring spins. The transfer matrix has the eigenvalues \([x \equiv \exp(Km)]\)

\[
\lambda_{\text{dis}} = x + 1/x + 2(m - 1), \quad \lambda_{\text{ord}} = x - 1/x, \quad \lambda = x + 1/x - 2, \tag{27}
\]

that are 1-fold, \(m\)-fold, and \((m - 1)\)-fold, respectively\(^{27}\).

We follow de Gennes\(^{28, 29}\) and provide an alternative and very useful interpretation of the above spin model in terms of a polymer system, in which each polymer has multiple bonds and loops. The valence at each site in a polymer must be even. (The presence of a magnetic field will allow odd valencies, which we do not consider here.) The high-temperature expansion of the PF, which is given by

\[
Z_N(K, m) = \sum K^B m^L, \tag{28}
\]

describes such a polymer system, with \(K \geq 0\), and \(m\) denoting the activity of a bond and the activity for a loop, respectively, and \(B\) and \(L\) denoting the number of bonds and the number of loops, respectively\(^{29}\). The empty sites represent solvent particles. The number of polymers and the number of bonds and loops in each polymer are not fixed and vary according to thermodynamics. In addition, there is no interaction between polymers, and between polymers and solvent particles, so that the polymer system in \(^{28}\) is an \textit{athermal} solution. The temperature \(T\) of the spin system does not represent the temperature in the polymer problem, as is well known\(^{28, 29}\). As we will see below, small \(x\) corresponds to high temperatures where the disordered phase is present, and large \(x\) corresponds to low temperatures where the ordered and possible SMS phases are present. Thus, decreasing \(T\) amounts to going towards the region where the ordered and metastable disordered phases are present. Let \(\omega\) denote the limiting value as \(N \to \infty\) of

\[
\omega = \left(1/N\right) \ln Z_N(K, m) + \ln(2m), \tag{29}
\]

where we have added an uninteresting constant to get rid of the prefactor in \(^{29}\). This is done because the number of microstates appears within the summation in the spin model PF in \(^{28}\). Thus, the inclusion of the prefactor will make the microstate entropy negative. The prefactor is, however, required for the polymer mapping.

The importance of the polymer mapping is that we can take \(m \geq 0\) to be a real number, even though non-integer \(m\) makes no sense for a physical spin. Thus, for non-integer values of \(m\), only the polymer system represents a physical system. For \(m = 1\), the axis model reduces to the Ising model, while for \(m \to 0\), it reduces to the a model of linear chains with no loops\(^{28, 29}\). The eigenvalue \(\lambda_{\text{dis}}\) is dominant at high temperatures for all \(m \geq 0\) and describes the disordered phase. Its eigenvector is

\[
\langle \xi_{\text{dis}} \rangle = \sum_i \langle i \rangle / \sqrt{2m},
\]
where $\langle 2k \rangle$ (or $\langle 2k+1 \rangle$) denotes the single-spin state in which the spin points along the positive (or negative) $k$-th spin-axis. It has the correct symmetry to give zero magnetization ($\rho = 0$). For $m \geq 1$, $\lambda_{\text{dis}}$ remains the dominant eigenvalue at all temperatures $T \geq 0$. For $0 \leq m < 1$, the situation changes and $\lambda_{\text{ord}}$ becomes dominant at low temperatures $T < T_c$, or $[x \geq x_c = 1/(1-m)]$ where $T_c$ is determined by the critical value $x_c \equiv \exp(Jm/T_c)$; there is a phase transition at $T_c$. The corresponding eigenvectors are given by the combinations

$$\xi^{(k+1)}_{\text{ord}} = \frac{\langle 2k \rangle - \langle 2k+1 \rangle}{\sqrt{2}}, \ k = 0, 2, \ldots, m - 1,$$

which are orthogonal to $\langle \xi_{\text{dis}} \rangle$, as can be easily checked. These eigenvectors have the symmetry to ensure $\rho \neq 0$. The remaining eigenvalue $\lambda$ is $(m-1)$-fold degenerate with eigenvectors

$$\xi^{(k+1)}_{\text{ord}} = \frac{\langle 2k \rangle + \langle 2k+1 \rangle - \langle 2k+2 \rangle - \langle 2k+3 \rangle}{\sqrt{4}}, \ k = 0, 2, \ldots, m - 2.$$

For $m > 0$, this eigenvalue is never dominant. For $m \to 0$, it becomes degenerate with $\lambda_{\text{dis}}$. Since the degeneracy plays no role in the thermodynamic limit, there is no need to consider this eigenvalue separately for $m \geq 0$.

We now consider the limit $N \to \infty$. The adimensional free energy per site, which represents the osmotic pressure\cite{8,30}, of the high-temperature equilibrium phase is $\omega_{\text{dis}}(T) \equiv \ln(\lambda_{\text{dis}})$. It can be continued all the way down to $T = 0$, even though the equilibrium osmotic pressure has a singularity at $x_c$. Similarly, $\omega_{\text{ord}}(T) \equiv \ln(\lambda_{\text{ord}})$ related to the low-temperature equilibrium phase can be continued all the way up to $T \to \infty$. To calculate the entropy density, we proceed as follows. The bond and loop densities are given by

$$\phi_B \equiv \frac{\partial \omega}{\partial \ln K}, \ \phi_L \equiv \frac{\partial \omega}{\partial \ln m},$$

which are needed to calculate the entropy per site of the polymer system

$$s^{(P)} = \omega - \phi_B \ln K - \phi_L \ln m;$$

the superscript is to indicate that it is the polymer system entropy, and is different from the spin system entropy $s^{(S)} = \partial T \omega/\partial T$. If we define $\omega$ without the last term in $s^{(P)}$, then $\phi_L$ and $s^{(P)}$ must be replaced by $(\phi_L - 1)$ and $(s^{(P)} - \ln 2)$, respectively. This will not affect any of the conclusions below.

In the following, we will be only interested in the polymer entropy. The proper stability requirements for the polymer system are

$$(\partial \phi_B/\partial \ln K) \geq 0, (\partial \phi_L/\partial \ln m) \geq 0,$$

as can easily be seen from $s^{(P)}$, and must be satisfied even for SMS. They replace the positivity of the heat capacity of the spin system, which no longer represents a physical spin system for $0 \leq m < 1$. It is easy to see from the definition of $s^{(P)}$ that $(\partial s^{(P)}_{\text{dis}}/\partial T)_m$ need not be positive, even if the conditions in $s^{(S)}$ are satisfied.
It should be noted that the Theorem 3 was for a canonical PF, whereas the polymer PF in (28) is an athermal grand canonical PF. The proof of the theorem can be easily extended to this or any other ensemble with similar results. Here, we will instead give a direct demonstration of the theorem. For this, we compute \( \omega \) as \( K \to \infty \) \((T \to 0)\) for the two eigenvalues \( \lambda_{\text{dis}} \) and \( \lambda_{\text{ord}} \). From (30), it is easy to see that \( \phi_{\text{B}} \to mK \) for both states as \( T \to 0 \). Thus, using \( \omega = s^{(P)} + \phi_{\text{B}} \ln K + \phi_{\text{L}} \ln m \), we have

\[
\frac{\omega_{\text{dis}}(T)}{\omega_{\text{ord}}(T)} \to 1 \quad \text{as} \quad T \to 0.
\]

This is in accordance with (25). This means that if the eigenvalue \( \lambda_{\text{dis}} \) is taken to represent the metastable phase above \( x_{c} \), its osmotic pressure must become equal to that of the equilibrium phase (described by the eigenvalue \( \lambda_{\text{ord}} \)) at absolute zero, in conformity with Theorem 3. We take \( \omega_{\text{dis}}(T) \) to represent the SMS osmotic pressure below \( T_{c} \). One can also check that \( T_{s}(S) \to 0 \), as \( T \to 0 \).

We will only discuss the disordered polymer phase below for \( 0 \leq m < 1 \). It is easily checked that the above stability conditions in (31) are always satisfied for \( \lambda_{\text{dis}} \); see, for example, the behavior of \( \phi_{\text{B}} \) in Fig. 2, where we have taken \( m = 0.7 \), and \( J = 1 \). Since the high-temperature disordered phase represents a physical system, it cannot give rise to a negative entropy \( s_{\text{dis}}^{(P)} \) above \( T_{c} \); however, its metastable extension violates it as shown in Fig. 2, where its entropy \( s_{\text{dis}}^{(P)} \) becomes negative below \( T_{K} \approx 0.266 \), which is lower than the transition temperature \( T_{c} \).

We now make an important observation. As \( m \) decreases (below 1), both \( T_{K} \) and \( T_{c} \) \((T_{K} < T_{c})\) move down towards zero simultaneously. As \( m \to 0 \), the equilibrium ordered phase corresponding to \( \lambda_{\text{ord}} \) disappear completely, and the disordered phase corresponding to \( \lambda_{\text{dis}} \) becomes the equilibrium phase. There is no transition to any other state. Thus, there is no metastability anymore. Consequently, there is no Kauzmann point since there is no other ordered state any more, as argued above. Thus, our exact calculation confirms our earlier conclusion that the existence of an ordered state is crucial for the existence of the entropy crisis. The existence of an ordered state sets the zero of the temperature scale by its minimum energy \( E_{0} \). This scale then sets the temperature \( T_{K} \) of the lowest SMS energy \( E_{K} > E_{0} \) to be positive. Thus, one must consider the ordered and the metastable states together.

We also observe that there is no singularity in \( \lambda_{\text{dis}} \) or \( \omega_{\text{dis}}(T) \) at \( T_{c} \), even though there is a phase transition there. Similarly, there is no singularity in \( \lambda_{\text{ord}} \) or \( \omega_{\text{ord}}(T) \) at \( T_{c} \). Thus, the thermodynamic singularity in the equilibrium free energy does not necessarily create a singularity in \( \omega_{\text{dis}}(T) \) or \( \omega_{\text{ord}}(T) \) at \( T_{c} \), as was discussed earlier. The existence of a singularity or spinodal at some other temperature is a different matter.

It should be noted that the eigenvalues \( \lambda_{\text{dis}} \) and \( \lambda_{\text{ord}} \) are independent of the size of the lattice. Therefore, they can be used to describe not only the disordered and ordered phases, but also the SMS, which is the continuation of the disordered phase, even for a finite \( N \). Thermodynamic limit is not necessary. For finite \( N \), \( Z_{\alpha}(K, m) < Z(K, m) \) and the inequality becomes an equality in
the sense of \[1\] only as \(N \to \infty\) for the proper choice of \(\alpha\) depending on the temperature.

### 6.2 Binary Mixture Model

We now consider a simple lattice model of an incompressible binary mixture of two kinds of particles A and B, to be represented by an Ising spin \(S\). The two spin states (+1 or up) and (−1 or down) represent the particles of two species A and B, respectively. As we are not interested in their phase separation, but in the possibility of a glass transition, we assume that their mutual interaction is attractive. In addition, we are interested in a first-order transition for conventional supercooling. We will, therefore, use an anti-ferromagnetic Ising model in zero magnetic field with both two-spin \((J > 0)\), and three-spin interactions \((J' \neq 0)\); the latter ensures that the melting transition is first order. In order to solve the model exactly, we consider a Husimi cactus made of squares, on which the model can be solved exactly[23]. We consider the simplest cactus in which only two squares meet at a site; they cannot share a lattice bond. The squares are connected so that there are no closed loops except those formed by the squares. The cactus can be thought as an approximation of a square lattice, so that the exact Husimi cactus solution can be thought of as an approximate solution of the square lattice model. There is a sublattice structure at low temperatures caused by the anti-ferromagnetic interaction: particles of one species are found on one of the two sublattices. We identify this ordered structure as a crystal. The interaction energy is

\[
E = J \sum SS' + J' \sum SS'S''.
\]  

(33)

The first sum is over nearest-neighbor spin pairs and the second over neighboring spin triplets within each square. In the absence of the three-spin coupling, the two-spin coupling gives rise to an antiferromagnetic (AF) ordering at low temperatures. For \(J' > (-J)\), the AF ordering remains the preferred ordering, while for \(J' < (-J)\), the ferromagnetic ordering is preferred. Therefore, we only consider \(J' > (-J)\) in the following. We set \(J = 1\) to set the temperature scale.

The model is solved recursively, as has been described elsewhere[23]. We label sites on the cactus by an index \(m\), which increases sequentially outwards from \(m = 0\) at the origin. We introduce partial PF’s \(Z_m(\uparrow)\) and \(Z_m(\downarrow)\), depending on the states of the spin at the \(m\)-th cactus level. It represents the contribution of the part of the cactus above that level to the total PF. We then introduce the ratio

\[
x_m \equiv Z_m(\uparrow)/[Z_m(\uparrow) + Z_m(\downarrow)],
\]  

(34)

which satisfies the recursion relation

\[
x_m \equiv f(x_{m+1}, x_{m+2}, v)/[f(x_{m+1}, x_{m+2}, v) + f(y_{m+1}, y_{m+2}, 1/v)],
\]  

(35)
where
\[ f(x, x', v) \equiv x^2 x'/u^4 v^4 + 2xx'yv^2 + x^2 yv^2 + u^4 x'y^2 + 2xyy' + y^2 y'/v^2, \quad (36) \]
with
\[ u \equiv e^\beta, v \equiv e^\beta J', y \equiv 1 - x, y' \equiv 1 - x'. \]

There are two kinds of fix-point solutions of the recursion relation that describe the bulk behavior\cite{23}. In the 1-cycle solution, the fix-point solution becomes independent of the level index \( m \) as we move towards the origin \( m = 0 \), and is represented by \( x^* \). For the current problem, it is given by \( x^* = 1/2 \), as can be checked explicitly by the above recursion relation in (35). It is obvious that it exists at all temperatures. There is no singularity in this fix-point solution. This solution corresponds to the disordered paramagnetic phase at high temperatures and the SMS below the melting transition. The other fix-point solution is a 2-cycle solution, which has been found and discussed earlier in the semi-flexible polymer problem\cite{7,8}, the dimer model\cite{31}, and star and dendrimer solutions\cite{32}. The fix-point solution alternates between two values \( x^*_1 \) and \( x^*_2 \) on two successive levels. At \( T = 0 \), this solution is given either by \( x^*_1 = 1 \), and \( x^*_2 = 0 \), or by \( x^*_1 = 0 \), and \( x^*_2 = 1 \). The system picks one of these as the solution. At and near \( T = 0 \), this solution corresponds to the low temperature AF-ordered phase, which represents the CR and its excitation at equal occupation, and can be obtained numerically. The 1-cycle free energy is calculated by the general method proposed in \cite{23}, and the 2-cycle free energy is calculated by the method given in \cite{7,32}.

For \( J' = 0.01 \), we find that \( T_M \approx 2.753 \), where there is a discontinuity in the entropy per site of 0.0168. The SMS below \( T_M \) represents SCL, whose entropy density, see Fig. 2, vanishes at \( T_K \approx 1.132 \), and whose specific heat (not shown) remains positive everywhere with a maximum at \( T \approx 1.26 \). At absolute zero, the entropy per site \( S_{\text{dis}} \approx -0.3466 \), while the CR entropy is zero, as expected. The CR and SCL free energies per site become identical (= 2J) at absolute zero in accordance with the Theorem 3. Thus, the free energy diagram we obtain in this case is similar to that in the inset in Fig. 1.

7 Discussion & Conclusions

7.1 Thermodynamic Criterion for Ideal Glass Transition

The work was motivated by a desire to identify a general thermodynamic mechanism for the glass transition. For this, we identify a general thermodynamic condition. This general principle has also been verified in some recent work on lattice models that have been carried out\cite{31,32}, and has its foundation in the original idea of the entropy crisis \( S_{\text{ex}} < 0 \) noted by Kauzmann, and is as follows. The entropy due to a set of coupled degrees of freedom, when properly defined either using quantum mechanics or by discretization as in a lattice model, can never be negative, since the number of configurations for a
given set of macroscopic quantities must be an integer \( \geq 1 \). Consequently, this condition of non-negative entropy \( S \) is nothing but the condition of reality. Its violation gives rise to the concept of absolute entropy crisis. It is in this sense we have used the entropy crisis in this work. Such a notion is more stringent than the Kauzmann criterion that \( S_{\text{ex}} \) be not negative, for which there is no thermodynamic justification, as we have argued in the Introduction. For the glass transition, we are interested in the set of coupled degrees of freedom that contains the configurational (i.e., positional) degrees of freedom. The entropy of such a set, regardless of whether quantum or classical mechanics is used in its calculation, is what we call the configurational entropy.

It should be noted that there are various other definitions of the configurational entropy in the literature. Many workers take \( S_{\text{ex}} \) to denote the configurational entropy. However, as said above, there is no thermodynamic basis for \( S_{\text{ex}} \) to be non-negative. So, it cannot play any role in a thermodynamic theory of glass transition. The landscape picture identifies the entropy \( S_{\text{IS}} \) of the inherent structure with the configurational entropy. Its vanishing is used to identify the glass transition. It is easy to see\(^\text{[33]}\) that for the classical configurational PF, the two entropies are related:

\[
S(T) = S_{\text{IS}}(T) + S_{\text{basin}}(T),
\]

where \( S_{\text{basin}}(T) \equiv \partial (T \ln Z_{\text{basin}}) / \partial T \) is the entropy arising from the average basin PF \( Z_{\text{basin}}(T) \) in the landscape picture. Thus, our criterion \( S(T) = 0 \) of the entropy crisis is also stringent than \( S_{\text{IS}}(T) = 0 \) in the landscape picture. Our criterion will also require \( S_{\text{basin}}(T) = 0 \), which can only occur at a temperature lower than the temperature at which \( S_{\text{IS}}(T) = 0 \). It should be noted that there is no kinetic energy contribution in \( S_{\text{basin}}(T) \) as the landscape picture deals only with the classical configurational PF; the translational degrees of freedom are decoupled in classical mechanics, as discussed above.

### 7.2 Continuum vs. Discrete Models

The best known example of classical models giving rise to negative entropy at low temperatures is the ideal gas. Similarly, classical real gases also give rise to negative entropy at low temperatures. This problem can be easily traced to the fact that we are treating the real and momentum spaces as continuum\(^\text{[31]}\).

Another well-known example is the Tonks gas of rods in one-dimension (no kinetic energy), which also gives negative entropy at high coverage\(^\text{[11, 31]}\). Here, the one-dimensional space is treated as continuum. On the other hand, it is well known that a classical lattice model will never give rise to negative entropy. Similarly, the random energy model\(^\text{[12]}\), which treats energy as continuum, gives negative entropy at low temperatures.

It is clear that the problem of negative entropy is not due to the classical nature of the systems, but due to the continuum nature of the model\(^\text{[13]}\). To ensure non-negative entropy, we must discretize the model, as we have discussed here. Once this has been done, the entropy crisis becomes a genuine crisis imposed by the reality condition as we have proposed earlier.
7.3 General Thermodynamic Mechanism for Ideal Glass Transition

The general thermodynamic mechanism of the ideal glass transition occurs in any system that has an ordered state, distinct from the high-temperature disordered state. The continuation of the free energy of the disordered state below the melting transition at $T_M$ gives the free energy of the stationary metastable state. We have shown that this continuation always gives rise to a stable free energy. For example, it gives rise to a non-negative heat capacity for $T \geq 0$. This SMS free energy $f_{\text{dis}}(T)$ becomes equal to $E_0$ at $T_{eq} > 0$, as the temperature is reduced. The energy continues to drop until finally, $f_{\text{dis}}(T) = E_0$ at $T = 0$. Since $f_{\text{dis}}(T) = E_0$ at $T = 0$ and at $T = T_{eq}$, it must have a maximum at some intermediate temperature $0 < T_K < T_{eq}$. The energy $E_K > E_0$ at $T_K$ because of positive heat capacity. The entropy is zero at $T_K$ and negative below $T_K$. Thus, the SMS over the range $(0, T_K)$ is unphysical and must be replaced by the ideal glass.

The above mechanism has been shown to be generic by the rigorous analysis, which is valid for classical and quantum systems. To the best of our knowledge, this result is the first of its kind and shows that the entropy crisis is genuine in those systems in which there is a more stable ordered state than the disordered SMS.

We have also considered models\cite{31} in which there are two possible transitions; one of them is from a disordered phase to an intermediate phase, and the second one at a lower temperature from the intermediate phase to an ordered phase. In this case, two possible SMS’s as the continuation of the disordered and intermediate phases emerge, with each extension giving rise to its own entropy crisis; in addition, both have the same free energy as $T = 0$ as the ordered phase. Thus, the mechanism is generic.

7.4 SMS & Exact Calculations

The transition between SMS and the ideal glass is not brought about by any thermodynamic singularity at $T_K$; rather, it is imposed by the reality requirement. To the best of our knowledge, the ideal glass state does not explicitly emerge as a phase in any calculation that has been carried out so far, including the two that are presented here. In this sense, this transition is a very special kind of transition, which does not seem to belong to the class of phase transitions in which various phases emerge in the calculation.

The two examples that we have presented here show the existence of SMS. Thus, they demonstrate that our hypothesis of SMS existence is not vacuous. Both examples also show genuine entropy crisis in SMS. Thus, they provide support for the violation of the reality condition in SMS at a positive temperature in exact calculations. We need to invoke an ideal glass transition at this temperature in each model.

The one-dimensional exact calculation is not a mean-field type calculation, and is presented not only to overcome the folklore that SMS’s exist only at the
mean-field level, but also to explicitly confirm the theorems. It is a model of a polymer system and confirms all the theorems. In particular, it shows that as \( m \to 0 \), the ideal glass transition disappears because there is no ordered state anymore. Hence, our results are not of mean-field nature.

The second example is also presented not only to overcome the folklore that frustration is crucial in the transition, but also to establish that entropy crisis is possible in systems containing small molecules, and not just polymers. There is no frustration in the Ising model because the cactus consists of squares. This example also confirms the theorems and the corollary.

Both examples show that the ideal glass transition occurs at a positive temperature and the energy \( E_K \) at that temperature is higher than \( E_0 \), the ideal CR energy at \( T = 0 \). This means that the ideal glass has a higher energy than the crystal at absolute zero, in conformity with the experiments.

### 7.5 Absence of Entropy Crisis in Equilibrium State

We now come to a very important consequence of our corollary. It is the following. The presence of an entropy crisis at a positive temperature implies that there must exist an equilibrium state for which no entropy crisis can exist. The equilibrium states in any system or model calculation, if carried out exactly, will never give rise to any entropy crisis at a positive temperature. This is because the lowest energy \( E_0 \) determines the lowest allowed temperature \( T = 0 \) in the system, even for a finite system. Since there cannot be any singularity in any finite-system equilibrium free energy, the latter should continue all the way down to \( T = 0 \) and the equilibrium entropy must remain non-negative at all temperatures; the latter can only vanish at \( T = 0 \). Thus, there would be no entropy crisis at a positive temperature in the equilibrium state. This will remain true as the thermodynamic limit is taken. Thus, no entropy crisis can occur at a finite temperature in the equilibrium state in that the entropy becomes negative below that temperature. However, it is possible that as \( N \to \infty \), the equilibrium free energy becomes horizontal, so that the entropy vanishes, over a non-zero temperature range \((0, T_C)\). Since the equilibrium free energy exists with non-negative entropy for all \( T \geq 0 \) for finite \( N \), the free energy must show a singularity at \( T_C \). While the system is frozen over the range \((0, T_C)\), its appearance is accompanied by a phase transition. (This should be contrasted with the existence of a Kauzmann point, below which the entropy becomes negative, but its appearance is not accompanied by any singularity in the SMS free energy. Replacing the unphysical SMS free energy below the Kauzmann point by a frozen state is done by hand; it does not emerge as part of the calculation.) Thus, we conclude that equilibrium state in any system will never show an entropy crisis at a positive temperature. The zero of the temperature scale is determined by the lowest possible energy \( E_0 \). If any exact calculation for the free energy or the entropy predicts an entropy crisis at a positive temperature, this will necessarily imply that there must exist another state, the equilibrium state, which will not show an entropy crisis.

This observation has been crucial in a recent investigation of a dimer model.
in which the disordered phase underwent a first-order transition to an equilibrium ordered phase. The ordered phase then gave rise to an entropy crisis at a lower temperature, which forced us to look for another equilibrium state, which was eventually discovered above the temperature where the entropy crisis was found, so that the crisis occurred in a metastable state (this time emerging from an intermediate ordered state) as we have suggested and followed the mechanism proposed here.

7.6 Landscape Picture

Finally, we wish to make connection of the ideal glass energy $E_K$ with the inherent structure in the landscape picture. The ideal glass at $T = 0$ in the canonical ensemble must be at a local minimum in the landscape. Hence, its energy must be the energy of the particular inherent structure. Since the ideal glass emerges at $T_K$, where $S(T) = 0$, we are forced to conclude that this inherent structure also represents SMS at $T_K$. This most certainly implies that SMS must be confined in the basin associated with the SMS inherent structure. This confinement must occur at a higher temperature (than $T_K$) where $S_{IS}(T) = 0$.

In conclusion, we have justified the mechanism that gives rise to an entropy crisis in metastable states in systems in which there exists a more stable phase. The generality of the mechanism is reflected in the generality of the validation of the mechanism, which is common in classical and quantum mechanical systems.

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irreducible PF in (1) containing the interaction energy in the rest of the paper. In quantum statistical mechanics for a system at rest and without rotation, the total Hamiltonian including the kinetic energy operator determines the PF in (1); thus, $S$ represents the total entropy $S_{\text{tot}}$ including the kinetic energy contribution.

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Figure Captions

1. Schematic form of the generic entropy functions for various possible states.
2. The bond and the entropy densities. Both models show an entropy crisis at a positive temperature.
