Energy Gap and the Ideal Glass as a Defective Crystal: A Lattice Model of Monatomic Systems

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Abstract

We use the cell model to justify the use of a lattice model to study the ideal glass transition. Based on empirical evidence and several previous exact calculations, we hypothesize that there exists an energy gap between the lowest possible energy of a glass (the ideal glass IG) and the crystal (CR). The gap is due to the presence of strongly correlated excitations with respect to the ideal CR; thus, one can treat IG as a highly defective crystal. We argue that an excitation in IG requires energy that increases logarithmically with the size of the system; as a consequence, we prove that IG must emerge at a positive temperature $T_K$. We propose an antiferromagnetic Ising model on a lattice to model liquid-crystal transition in a simple fluid or a binary mixture, which is then solved exactly on a recursive (Husimi) lattice to investigate the ideal glass transition, the nature of defects in the supercooled liquid and CR analytically, and the effects of competing interactions on the glass transition. The calculation establishes the gap. The lattice entropy of the supercooled liquid vanishes at a positive temperature $T_K > 0$, where IG emerges but where CR has a positive entropy. The macrostate IG is in a particular and unique disordered microstate at $T_K$, just as the ideal CR is in a perfectly ordered microstate at absolute zero. This explains why it is possible for CR to have a higher entropy at $T_K$ than IG. The demonstration here of an entropy crisis in monatomic systems along with previously known results strongly suggests that the entropy crisis first noted by Kauzmann and demonstrated by Gibbs and DiMarzio in long polymers appears to be ubiquitous in all supercooled liquids.
I. INTRODUCTION

A. Glass as a Stationary Metastable State (SMS)

A common feature of almost all crystallizable materials is that they can become glassy, a state that is metastable. The true equilibrium state corresponds to its crystalline state (CR). The glass is obtained by cooling the supercooled liquid (SCL). The metastable states (MSs) have higher free energies than the corresponding equilibrium state (EQS) and violate the fundamental thermodynamic property that the equilibrium free energy be minimized or the equilibrium partition function (PF) be maximized. Even at absolute zero, glasses are empirically found to have higher energies compared to their crystalline form because of their metastability. We call this difference in their energies the energy gap. The existence of glasses cannot be rigorously demonstrated by equilibrium statistical mechanics, in which one considers all microstates in the PF. We need to go beyond it to explain their existence. One way is to restrict the microstates in the PF to be only disordered to describe glasses. As a consequence, many standard results of equilibrium thermodynamics will not hold for metastable states, even when they are manipulated to exist for an abnormally long time, a situation that commonly occurs for glasses.

Stable and abnormally long lasting MSs can be easily prepared; we only have to recall the stability of medieval glasses. They also appear in many mean-field theories including the van der Walls equation such as the Bragg-Williams theory and in exact calculations. They emerge solely because we abandon the free energy minimization principle in the calculation. The violation of this principle can still lead to a time-independent stable solution, except that it is metastable. The stability only requires the specific heat, compressibility, etc. to be non-negative. Such mathematically stable time-independent solutions in theoretical models imply that they will never decay. We therefore call them stationary metastable states (SMSs) to distinguish them from MSs that are encountered in experiments and that usually change with time. In experiments, MSs emerge by the very nature of preparing the system such as a fast quench, after which they undergo structural relaxation towards their respective SMS associated with the stable solution. In this work, we will assume that there is only one SMS at a given temperature and volume. A complete understanding of time-dependent MSs is not possible without a comprehensive understanding of corresponding
SMSs. Thus, in this work, we focus our attention on investigating SMSs only. This stable solution has the lowest free energy among all metastable states. It is time-independent, and represents an "equilibrium state" similar to the equilibrium liquid (EL), except that the former is metastable; the true equilibrium state is CR. In the following, we will call a SMS an equilibrium state, even if it is a metastable state. This should cause no confusion. All other MSs represent time-dependent non-equilibrium states (NEQSs). As the system relaxes from a NEQS towards SMS, the energy continues to decrease. Thus, the energy gap of a SMS cannot be larger than that for a NEQS.

There are usually two different mechanism operative in MSs. The "fast" mechanism (time scale $\tau_f$) creates a metastable state in the system, followed by a "slow" mechanism (time scale $\tau_s$) for nucleation of the stable phase and the eventual decay of the metastable state. For an MS to exists for a while, we need to require $\tau_s > \tau_f$. The time-dependent NEQSs include not only states that will eventually turn into equilibrium states (such as crystals), but also states that will eventually turn into SMSs (such as glasses) as we wait infinitely long (in principle), depending on how they are prepared. To study glass dynamics, we need to compare the two time scales with the longest feasible experimental observation time $\tau_{exp}$.

From the experimental point of view, the inequality $\tau_s >> \tau_{exp}$ for supercooled liquids is almost equivalent to the long time, i.e. the stationary limit $\tau_s \to \infty$ of metastable states; we again appeal to the stability of medieval glasses. Thus, to a first approximation, we can treat real glasses and SCLs as SMSs, states which never decay. (According to Maxwell, this can, in principle, be achieved by ensuring that the equilibrium state nuclei are absent in MSs.) Above the glass transition, SCL is an equilibrium state in the sense of a SMS. Thus, we will assume the existence of these SMSs, as they play a central role in our modeling and understanding of glass formers; see the above discussion. This allows us to use the PF formalism to study a SMS. The study of SMSs, which can be carried out using the basic principles of statistical mechanical formalism, though modified by imposing some restrictions as described later, still has a quite useful predictive value. The actual dynamics that leads to such a state will not be our focus here, even though it is important in its own right.
B. Entropy Crisis

The excess entropy (to be correctly replaced later by the communal entropy in a continuum model or the entropy in a lattice model; see Sect. II B) of SCL exhibits a rapid drop below the melting temperature $T_M$, and eventually vanishes at some temperature $T = T_K < T_M$. It will become negative if extrapolated to lower temperatures. A negative communal entropy is considered unphysical. Thus, the extrapolation gives rise to an entropy crisis at $T_K$. An ideal glass transition is invoked to avoid this crisis at $T_K$. In the limit of zero cooling rate (not accessible in experiments or simulations, but accessible in a theoretical setup) in the metastable region, metastable states are nothing but SMSs, and can be described by "equilibrium" statistical mechanics by restricting the allowed microstates to be disordered; microstates leading to the crystalline state are not allowed. In experiments, the extrapolated excess entropy of many glassy materials at $T = 0$ is found to have a non-zero value depending on the rate of cooling. This does not rule out the possibility that the entropy of the hypothetical "stationary" glass vanishes in the limit of zero cooling rate at a positive temperature. Furthermore, the amount of entropy discontinuity at melting is not important for the existence of an ideal glass transition; all that is required is the existence of a supercooled liquid relative to a CR in which the entropy is very small. The latter can happen either by a very large latent heat or by a rapid drop in its entropy; see the behavior of CR entropy in Figs. 5 and 6.

Demonstrating an entropy crisis for supercooled liquids in a restricted formalism has been one of the most challenging problems in theoretical physics because of the inherent approximation involved in most calculations. An entropy crisis in long polymers was theoretically demonstrated almost fifty years ago by Gibbs and DiMarzio to support the entropy crisis as a fundamental principle underlying glass transitions in long polymers. Their work was later criticized by Gujrati and Goldstein for its poor approximation, and doubt was cast on whether the entropy crisis in long polymers was genuine. The situation changed when in a recent work, Gujrati and Corsi established the existence of an entropy crisis in long polymers by using a highly reliable approximate approach. This was very important as the idea of Gibbs and DiMarzio has been pivotal in shaping our thinking about the ideal glass transition. Recently, we have also succeeded in demonstrating the entropy crisis in a dimer model containing anisotropic interactions.
C. Current Goal

Our goal in the present work is two-fold. First, we demonstrate the crisis in simple isotropic fluids containing monatomic particles. The second aim is to understand the nature of a general glassy state by investigating monatomic glass formers and the lessons learned from our previous investigations. Study of monatomic glass formers also allow us to obtain a better understanding of the glassy structure (defects therein) whose accurate representation still remains challenging. For the general investigation, we propose a generic model of the entropy, which is consistent with our previous exact calculations and the calculation presented here for monatomic glass formers. The slow relaxation in SCLs is similar to that observed in ordinary spin glasses, whose important features are their geometrical frustration and competition. We will, therefore, also investigate whether the competition and frustration play an important role in promoting the glassy behavior in monatomic glass formers.

It should be noted that frustrated antiferromagnets (AF) and spin glasses do not usually possess long range order at low temperatures because of a highly degenerate ground state and their glassy behavior is brought about by the presence of frustration or quenched impurities and is somewhat well understood. In contrast, supercooled liquids require a unique ground state, the crystal. This distinguishes the glassy behavior in supercooled liquids and requires considering an unfrustrated AF model as a paradigm of simple fluids or alloys in this work. We consider a pure (no frustration or quenched impurities) AF Ising model, which possesses a unique ordered state, which is identified with CR, so that supercooling can occur. This then results in a glassy state. The use of a magnetic model to study glassiness is highly desirable as magnetic systems have been extensively studied in theoretical physics and are well understood at present. This makes interpreting the results very easy and transparent. We are not aware of any simple model calculation to date to justify glassy states in a pure AF model. The model allows us to investigate the defects that occur in the ideal glass (with respect to the corresponding crystal). We also find that the competition considered in this work inhibits instead of promoting the glass transition, which is a surprising result.
D. Layout

The layout of the paper is as follows. In the next section, we use the celebrated cell model of fluids to argue that it is the communal entropy that should determine the location of the glass transition, in which the glass "melts" from its localized state into a delocalized liquid state. It is shown that a lattice model is sufficient to determine the glass transition. The thermodynamics of metastability, the role of the energy gap on the entropies of ordered and disordered states, and the possible free energies of the two states are discussed in Sect. III. The conjectural form of the entropy is based on the work of Gibbs and DiMarzio and exact calculations from our group. The lattice model is introduced in Sect. IV and is analytically solved in Sect. V. The results are presented in Sect. VI. This section forms the core of the present work and contains important results including the demonstration of an energy gap, the existence of an ideal glass transition, the discussion of defects and the nature of the ideal glass as a single disordered microstate. The last section contains a brief summary of the work.

II. CELL MODEL

A. Localization or Confinement

One of the most important property of SCLs at low temperatures is that glasses and CRs have very similar vibrational heat capacities below $T_g$, except that glasses have higher potential energies than the corresponding CRs. Let $E_{\text{NEQS}}$ denote the lowest possible energy of a NEQS such as a glass and $E_0$ the energy of the ideal crystal at $T = 0$. Then, we empirically have

$$E_{\text{NEQS}} > E_0. \quad (1)$$

The difference

$$\Delta_G \equiv E_{\text{NEQS}} - E_0 > 0 \quad (2)$$

is called the energy gap. Otherwise, glasses and crystals are confined to execute quite similar vibrations (not necessarily harmonic) within their potential wells or basins, although their minima are at different energies, to a first approximation, notwithstanding the clear evidence to the contrary. All that is important is that both glasses and crystals exhibit
FIG. 1: Cell representation of a small region of disordered (a) and ordered (b) configurations at full occupation: each cell contains a particle. Each cell representation uniquely defines a potential well or basin in the potential energy landscape. Observe that while each particle is surrounded by four particles in the ordered configuration, this is not the case for the disordered configuration. We have shown a higher volume for the disordered configuration, as found empirically; see later.

localized motion. This property has led to the enormous popularity of the potential energy landscape picture, originally proposed by Goldstein\textsuperscript{25} to investigate glass transition in a system consisting of \( N \) particles. The potential energy \( E(\{r\}) \) as a function of the set \( \{r\} \) of particles' positions uniquely determines this landscape. A glass is confined to one of the myriads of potential wells, while the crystal is most commonly believed to be confined to just one potential well. The number of these basins determines the basin entropy, and is a measure of the entropy, which Goldstein identifies as the residual entropy\textsuperscript{24}.

A glass is SCL trapped in one of the many basins at \( T_g \), and executes vibrations within this potential well. The resulting glass can be characterized by the properties of this basin\textsuperscript{1,25}, which determine the average configuration of the glass in that basin. The high barriers of these potential wells also provide high stability to very slowly cooled SCLs, at least near \( T_g \), and are responsible for the strong inequality \( \tau_s >> \tau_{\text{exp}} \). This also implies that barriers to the formation of stable nuclei must also be extremely high in SCLs. This was first argued by Goldstein in his seminal work on viscous liquids\textsuperscript{25}. This picture of slowly-cooled SCLs

\[ \text{FIG. 1: Cell representation of a small region of disordered (a) and ordered (b) configurations at full occupation: each cell contains a particle. Each cell representation uniquely defines a potential well or basin in the potential energy landscape. Observe that while each particle is surrounded by four particles in the ordered configuration, this is not the case for the disordered configuration. We have shown a higher volume for the disordered configuration, as found empirically; see later.} \]
allows us consider the liquid cell model of Lennard-Jones and Devonshire, see Fig. 1, and its various elaborations. We show a cell representation of a dense liquid in (a) and of a crystal in (b). Each cell is occupied by a particle in which it vibrates. The regular lattice in (b) is in accordance with Einstein’s model of a crystal. In the liquid state, this regularity is absent. A defect in the cell representation corresponds to some empty cells, as shown in Fig. 2. We consider the (configurational) partition function $Z(T, V)$

$$Z(T, V) \equiv \frac{1}{\nu_0^N N!} \int e^{-\beta E} d^N \{r\} \equiv \int W(E, V) e^{-\beta E} dE/\epsilon_0,$$

in the canonical ensemble at temperature $T$ (measured in the units of the Boltzmann constant $k_B$; this amounts to effectively setting $k_B = 1$); $\beta \equiv 1/T$ is the inverse temperature, and $W(E, V)dE/\epsilon_0$ represents the number of distinct configurations with potential energy in the range $E$ and $E + dE$; $\nu_0$ and $\epsilon_0$ represent some small-scale constant volume such as the cell volume, and some energy constant, such as the average spacing between vibrational energy levels of a single particle in its cell in Fig. 1(b) at $T = 0$. We set $\nu_0 = 1$ and $\epsilon_0 = 1$ in this work.

One should carefully make a distinction between a quantity and its configurational com-
ponent by adding a subscript "T" to the quantity. For example, $S_T(T, V)$ will denote the (total) entropy, while $S(T, V)$ the configurational part of $S_T(T, V)$. The microcanonical configurational entropy is given by the Boltzmann relation so that:

$$S(E, V) \equiv \ln W(E, V)dE/\epsilon_0 \simeq \ln W(E, V) \geq 0.$$ 

The average energy $\bar{E} = E(T, V)$ is used to give the canonical configurational entropy $S(T, V) \equiv S[E(T, V), V]$. The slope of the entropy at $\bar{E}$ is related to the inverse temperature by the standard relation valid at equilibrium

$$(\partial S/\partial E)_V |_{\bar{E}} = \beta. \quad (4)$$

This entropy differs from the total entropy $S_T(T, V)$, which is the entropy associated with the total PF $Z_T(T, V)$ where the kinetic energy (KE) is also included.\textsuperscript{18,19,20,30} The entropy contribution $S_{KE}(T)$ due to the kinetic energy is the same for all systems as it is independent of the interactions and volume. For this reason, we do not have to include $S_{KE}(T)$ in any investigation of metastability. We only consider the configurational degrees of freedom from now on. For the same reason, there is also no need to explicitly show the dependence on $V$. The configurational part of the Helmholtz free energy is given by $F(T) \equiv -T \ln Z(T)$, where we have suppressed $V$.

**B. Communal Entropy**

The communal entropy is defined as the difference between the configurational entropy $S(T)$ of the system and the entropy $S_b(T)$ when the particles are confined in their cells,\textsuperscript{31} i.e., the basin (we suppress showing the $V$-dependence):

$$S_{\text{comm}}(T) \equiv S(T) - S_b(T) \geq 0. \quad (5)$$

The communal part of the free energy is given by

$$F_{\text{comm}}(T) \equiv F(T) + TS_b(T) = E(T) - TS_{\text{comm}}(T). \quad (6)$$

The communal entropy is the entropy due to the deconfinement of the system from the basin. It is a measure of the diffusional contribution to the total entropy as opposed to the
vibrational entropy. Accordingly, it vanishes when the system is confined in a basin such as in Fig. 1(a). Let $T_K > 0$ denote the temperature when this happens for SCL:

$$S_{\text{comm}}^{\text{SCL}}(T_K) \equiv 0. \tag{7}$$

Several authors identify the communal entropy as the configurational entropy. We, however, reserve this name for the entropy associated with the configurational partition function $\{3\}$. Another appropriate term for the communal entropy is the residual entropy. Here, we will stick with the term communal entropy, which conveys directly the idea of delocalization. From now on, we will simply call any configurational quantity $Q(T)$ such as $S(T)$ as the quantity; we will refer to $Q_T(T)$ as the total quantity.

As noted in Sect. III, it is a common assumption that CR is also confined to a single basin such as the one shown in Fig. 1(b). If the assumption holds, then the confinement will occur at some $T_{\text{CR}} > 0$:

$$S_{\text{comm}}^{\text{CR}}(T_{\text{CR}}) \equiv 0. \tag{8}$$

As we will see later in Sect. VI, this does not happen due to the presence of defects that emerge in CR. Thus, the CR lattice entropy (the communal entropy) vanishes only at absolute zero. We will also see there that the defects in IG are strongly correlated, making them different in nature from those in CR. We will discuss this issue further in Sects. III and VI.

In confined or localized states, particles only occupy positions that are within their individual cells. Let us focus on a SCL localized into one such basin. Let the minimum of the basin energy be $E_K$. It corresponds to the average state in the basin in which each particle has its average position. Any deviation from these positions will only raise the potential energy. The relevant average state in the basin at $T = T_K$ remains unchanged below $T_K$ and continues to represent the average state of the system. In other words, the average state of the system remains frozen in this \textit{inert average state} below $T_K$ and is called the \textit{ideal glass} (IG). This localization and freezing of the average state to IG is called the ideal glass transition. Thus, the vanishing of $S_{\text{comm}}(T)$ in (7) is taken as the condition for the formation of an IG due to its localization or confinement in a single basin, and the temperature $T_K$ at which this occurs is called the ideal glass transition temperature or the Kauzmann temperature, to honor the pioneering contribution of Kauzmann in the field of supercooled liquid, even though the term is commonly used to denote the temperature where the CR
and SCL have the same entropy. This issue has been discussed elsewhere\textsuperscript{19,20,30} to which we refer the reader for additional information.

**Remark** In a lattice model, particles do not deviate from their fixed lattice positions. Consequently, the total entropy in the lattice model is purely communal in nature.

Thus, a lattice model can be effectively used to analyze the average state of a glass former in real continuum space. Accordingly, we do not feel guilty about using lattice models here for which exact calculations can be carried out. As the entropy of the IG is zero\textsuperscript{29} it means that the macrostate corresponding to IG is really a microstate. In other words, the IG at $T_K$ refers to a particular disordered microstate of energy $E_K$ in a lattice model. This is no different from the ideal CR at absolute zero, which is also in a the perfectly ordered microstate.

Since the heat capacity is non-negative, $S(T)$, and $E(T)$ are monotonic increasing function of $T$, and must have their minimum values at absolute zero. Assuming CR to be the stable phase at absolute zero, we conclude that it must be in the state with the lowest possible energy $E_0(V)$. This follows from the Nernst-Planck postulate\textsuperscript{32}

$$TS_{CR}(T, V) \rightarrow 0 \text{ as } T \rightarrow 0,$$

so that

$$F(T = 0, V) = E_0(V).$$

As long as the heat capacities of various phases, stable or metastable, remain non-negative, and we will see that this is true, all higher energies will correspond to temperatures $T > 0$. As the lowest possible energy of the glass is $E_K > E_0$, this energy gap will suggest that the SCL will get into the IG microstate at $T_K > 0$. We have seen it to be true in all of our exact calculations so far\textsuperscript{9,10,17,18,19,20} it is also true in the present calculation, as we will see later in Sect. \textsuperscript{VI}. The calculation by Gibbs and DiMarzio\textsuperscript{15} is also consistent with this claim.
III. THERMODYNAMICS OF METASTABILITY

A. Schematic Communal Entropy

There are no general arguments\textsuperscript{2,33,34} to show that thermodynamically stable states must always be ordered, i.e., periodic. The remarkable aperiodic Penrose tilings of the plane, for example, by two differently but suitably shaped tiles are stable. It is found empirically that the volume (or the energy or enthalpy) of a glass, or more generally, an NEQS at absolute zero is higher than that of the corresponding crystal; see\textsuperscript{13} for example for a careful analysis of data. The energy gap is also seen in the original calculation of Gibbs and DiMarzio,\textsuperscript{15} and many exact calculations carried out in our group.\textsuperscript{9,10,16,17,18,19,20} Here, we will focus on the potential energy for which the above observation is in accordance with (1); see Fig. 3. (There will be no energy gap if $E_{\text{NEQS}} = E_0$.) According to (1), there must be many defects in the glass relative to the crystal even at absolute zero to account for this difference in the energy (or enthalpy). The number and nature of these defects must ensure that the glassy state is not only disordered but also has a very small amount of communal entropy. The value of $E_{\text{NEQS}}$ depends on the rate of cooling $r$. As $r$ decreases, this energy falls and approaches a limiting value $E_K \leq E_{\text{NEQS}}$, which is still higher than $E_0$; see Sect. V. As CR is heated, its energy rises due to the defects, but their densities is much smaller in the crystal to leave it ordered; compare it with the corresponding glass at the same temperature, which is disordered and has much higher energy. As a consequence, one can treat a glass as a highly defective crystal\textsuperscript{37} with so many defects to the point that the crystal becomes disordered.

To form a glass, crystallization must be avoided either by ensuring that the material does not have time to become crystalline or by suppressing the mechanism to form a crystal. As glasses, or more generally NEQSs, are formed under some sort of constraints (crystallization is forbidden in the case of glasses), their (communal) multiplicity $W_{\text{NE}}(E)$ (which may be a function of time, but we do not show it) must not be greater than $W_{\text{EQ}}(E)$ of the corresponding equilibrium state, so that we must always have

$$S_{\text{NE}}(E) \leq S_{\text{EQ}}(E);$$

see Fig. 3 for fixed $V$. The curve OHH’D (with straight segment HH’) represents $S_{\text{EQ}}(E)$ and the curve GF represents $S_{\text{NE}}(E)$. In time, the curve GF will move upwards towards
FIG. 3: Schematic form of generic communal entropy functions defined in (5) as continuous and concave functions of $E$ for a fixed volume $V$ for various possible states, and the resulting continuous and concave Helmholtz free energies in the inset. Note the presence of an energy gap ($\Delta G > 0$). This form, which is shown in an exaggerated fashion to highlight the distinction, will be justified by our results in Sect. VI. The form is also consistent with all known exact calculations from our group.\textsuperscript{17,18,19,20,35} The point O' represents the point where the free energy DO'CKO of the liquid in the inset is equal to the free energy of the crystal at O (absolute zero). The point A on DO'CKO in the inset is slightly below the melting temperature $T_M$, where it crosses the crystal free energy OAB.

OHH'D: it either converges to it if crystallization occurs, or to KCAD if it is forbidden. This is consistent with the second law of thermodynamics: As the constraints are removed, the entropy of a closed system (fixed $E, V$) cannot decrease in time; it can only increase or remain constant. It is interesting to note that this entropy form is consistent with the calculation of Gibbs and DiMarzio.\textsuperscript{15}

From now on, we will only consider a lattice model in which the entropy is the communal entropy shown schematically in Fig. 3. The segment H'D represents the entropy of the liquid, the disordered phase, and is determined by the multiplicity $W_{\text{dis}}(E)$ of disordered
configurations. The segment OH represents the entropy of the crystal, the ordered phase, and the entropy is determined by the multiplicity $W_{\text{ord}}(E)$ of ordered configurations. Because of the straight segment HH', the equilibrium entropy $S_{\text{EQ}}(E)$ is a singular function, which is then reflected in a singular equilibrium free energy at the melting temperature $T_M$; the latter is given by the inverse of the slope of HH', see \cite{1}. (It should be stressed that the actual value of the energy discontinuity at melting, reflected by the tangent construction HH', is not relevant for the investigation of metastability.) Let $E_{\text{CR,M}}$ and $E_{\text{EL,M}}$ denote the energies of the coexisting phases CR and EL at $T_M$; see points H and H' in Fig. 3. It is hard to imagine that the ordered and disordered configurations terminate at $E_{\text{CR,M}}$ and $E_{\text{EL,M}}$, respectively. Thus, we will assume that the curve KCAH'D represents the entropy

$$S_{\text{dis}}(E) \equiv \ln W_{\text{dis}}(E)$$

of the disordered states in the system even below $E_{\text{EL,M}}$. Similarly, we will assume OHAB to represent the entropy

$$S_{\text{ord}}(E) \equiv \ln W_{\text{ord}}(E)$$

of the ordered states in the system even above $E_{\text{CR,M}}$. The entropy then has two different branches KCAD and OHAB, rather than a single function given by OHH'D. We only require that the branches be continuous and concave\cite{36}. The existence of the two branches requires that we are able to distinguish between disordered and ordered states. After all, the glassy state is formed by disordered states. So, making such a distinction is not merely an academic curiosity; it is of vital importance for our understanding of how and why glasses are formed.

\subsection*{B. Non-zero $T_K$}

As we wait longer and longer, NEQS will approach its two possible stationary limits: EQS or SMS. In the process, the energy $E_{\text{NEQS}}$ will continue to decrease.\cite{11} It will converge to $E_0$ if NEQS approaches CR and there will be no energy gap; otherwise, it will converge to some higher energy $E_K$ with an energy gap, if NEQS converges to IG/SCL. The presence of the gap will turn out to imply a non-zero $T_K > 0$. The following provides another and more illustrative proof of this claim for the point K in Fig. 3. The energy gap requires a large amount of defects to give rise to a disordered state associated with K, where the entropy also vanishes. The defects at K must be very special in that they cannot be uncorrelated.
like point-like defects that appear in CR. They must be strongly correlated not only to make the particular IG microstate disordered, but also to ensure that one cannot obtain other disordered microstates of the same energy by simply exchanging distinct defects. The latter condition must hold for IG to have zero entropy. Uncorrelated distinct defects can be exchanged without changing the energy to generate many distinct microstates. In the process we raise the entropy at $K$, which contradicts that the entropy vanishes there. Thus, we conclude that the defects in IG are strongly correlated.

Any defects, whether local (finite in size or independent of the lattice size $N$) or non-local (growing with the lattice size $N$ so that it becomes infinitely large in the limit $N \to \infty$), each can be created in in $\sim N$ different ways by simply moving its ”center-of-mass” to any of the $N$ lattice sites. One may also be able to rotate the defect without affecting the energy. Thus, the gain in the entropy is

$$\Delta S|_V \sim \ln N.$$  

(10)

This remains true whether we consider an ordered state or a disordered state.

Let us now follow the consequence of the defects. The uncorrelated point-like defects in a perfect CR are local defects that each require a small non-extensive energy of excitation without destroying the order completely. Using (10) for a defect, we have for their ratio

$$\left( \frac{\Delta E}{\Delta S} \right)_V \sim 1/\ln N,$$

(11)

which vanishes as $N \to \infty$. This explains, see (1), why the corresponding temperature of the perfect CR is $T = 0$. On the other hand, the defects in a glass are highly correlated. If these defects were of finite size, they require a finite amount of energy of excitation. Then the above argument applied to CR will suggest not only that IG can only emerge at absolute zero, but also that one can also lower the energy of IG by removing some of these defects. Lowering of the energy has two very important consequences. The first one violates the condition that $E_K$ is the lowest energy of IG. The second one is that removal of the defects can be done in many ways to make the entropy of the lower energy state non-zero, which then violates the concavity condition. Thus, we conclude that the defects in IG are not finite in size. Accordingly, their creation must raise the energy that cannot remain finite. Let us assume that the excitation energy $\propto N^p$ for a defect, where $1 \geq p > 0$. Using (10)
for a defect, we find the ratio
\[
\left( \frac{\Delta E}{\Delta S} \right)_V \sim \frac{N^p}{\ln N} \to \infty,
\]
(12)
as \(N \to \infty\) provided \(p > 0\). From (4), this will then correspond to an infinite temperature \(T_K\), which is certainly not a physically relevant situation. The only meaningful way one can have non-localized defects in IG is to have the excitation energy due to a defect to be
\[
\Delta E|_V \sim \ln N.
\]
(13)
In this case and using (10), the ratio
\[
\left( \frac{\Delta E}{\Delta S} \right)_V = \text{constant} > 0
\]
(14)
as \(N \to \infty\). It now follows immediately that the IG transition occurs at a non-zero and finite temperature, which we identify with \(T_K\). This proves our claim.

It should be emphasized that the proof of the claim is based on the existence of the energy gap. Thus, its validity provides a verification of our gap model. The claim turns out to be consistent with the results in Sect. VI. It is also consistent with our previous exact results.\textsuperscript{17,18,19,20,35} The following thermodynamic argument also supports the claim. The vanishing of the entropy at \(K\) means that the free energy has a maximum there at \(T_K\). Thus, except in some special cases, the free energy is quadratic in \(T\) at \(T_K\) in the leading order:
\[
F(T) = F(T_K) - a(T - T_K)^2 + \cdots
\]
where \(a > 0\) is a constant in \(T\). Thus, both the entropy and the excitation energy are linear in \((T - T_K)\) in the leading order, so that they are proportional as required by (14). All these verifications provide a strong validation of the energy gap model. As the slope of DAK in Fig. 3 is finite at \(K\), this allows the possibility of continuing DAK to the region below \(E_K\), where one will encounter a negative communal entropy. This possibility of the extension of DAK below \(K\) is why various calculations give this unphysical branch.\textsuperscript{15,17,18,19,20,35}

The strong correlations produced by these non-localized defects in IG must be of such a nature that one cannot reduce the energy of the IG microstate below \(E_K\). How does this happen can only be answered after we can identify the IG microstate, which at present is an unsolved problem. It is hoped that the present simple but analytical solution presented in Sect. V will be a first step towards this goal. It should also be said at this point that the
above discussion for IG is not applicable to real glasses described by the curve FG in Fig. 3. The central point in the above discussion was the impossibility of generating disordered microstates of energies lower than $E_K$. However, this is not applicable at the point G, since one can certainly produce disordered microstates of energies lower than $E_{\text{NEQS}}$. As a consequence, the defects in real glasses are going to be local and not non-local. Accordingly, the temperature at G will be zero; see (11). Even the entropy there does not have to vanish.

C. Order Parameter

We have already argued elsewhere\textsuperscript{19} that the ideal glass transition is a continuous transition at which the free energy will exhibit a thermodynamic singularity. The result is based on the form of entropy shown in Fig. 3. Therefore, it is necessary to identify an order parameter for the IG transition. For this, we turn to the melting of crystals into liquids, which is similar (but not identical) to the "melting" of glasses into SCLs. This will require leaving the lattice model for a while. According to the Lindemann criterion of melting,\textsuperscript{39} a crystal melts when the mean-square displacement $r^2$ becomes so large that the atoms start to get into each other's cells to the point that they begin to diffuse over a large distance, and the melting initiates. If $a$ denotes the interatomic distance in the crystal, then the melting proceeds when $r^2 = c_L a^2$, where $c_L$ is Lindemann’s constant and is expected to be the same for crystals with similar structure. It should, however, be pointed out that the criterion is expected to be valid only for those systems that have simple crystalline structures. For particles obeying Lennard-Jones potential, Jin and coworkers\textsuperscript{40} have tested the validity of the criterion by considering 6912 Lennard-Jones particles. The value of $c_L$ is estimated to be $\simeq 0.12-0.13$ at equilibrium melting, as expected. As the temperature is raised towards the melting temperature, clusters of correlated particles of various sizes are formed. At the melting, the correlations become too strong and the density of defects becomes large enough that the crystal melts. These defects in CR are necessary to melt it and require a macroscopic energy $\Delta E \propto N$ to be created, which is reflected in the energy discontinuity. The associated entropy discontinuity $\Delta S \propto N$ is such that the ratio

$$\left( \frac{\Delta E}{\Delta S} \right)_V = T_M,$$
compare with (14), which follows from the equality of the free energy $F$ in the two phases in coexistence. This equation should be compared with (4). The equality of the two follows from the linear or tangent construction which gives rise to $HH'$ in Fig. 3. If we now treat a glass as a defective crystal\footnote{37} with a disordered cell representation, then it is not hard to imagine that a similar criterion can be applied to the "melting" of a glass into its SCL state. We will pursue this analogy a bit further below.

The so-called melting of an ideal glass into a SCL is nothing but a localization-delocalization transition, as discussed in Sect. II A, similar to the melting transition. As the temperature is raised, the IG becomes deconfined and begins to probe via diffusion other basins corresponding to different cell representations, thereby giving rise to the $\alpha$ relaxation. We can make this process somewhat quantitative\footnote{44} by considering a particle at some average position $r_0$ within its cell. We average the square of its displacement. At low temperatures where it is confined within its cell, the particle does not diffuse away from the original point $r_0$; it merely undergoes vibrations within its cell. Let us introduce a certain length $b$ characterizing the average size of the cell. Then, $r^2 \leq c_G b$, with $c_G < 1$ a parameter that depends on the system under investigation, will characterize a "solid-like" atom (S) in that the particles satisfying this constraint are only allowed to vibrate about their equilibrium position $r_0$ within their cells. This will be the situation in the IG, in which the particles do not diffuse out of their cells. On the other hand, $r^2 > c_G b$ will describe a "liquid-like" atom (L) in that the particles escape the neighborhood of $r_0$ by diffusion and will give rise to a collective motion. Thus, we can classify the atoms as L or S, thereby reducing the system to a "fictitious" binary mixture of L and S particles. This scenario was conjectured by us a while back\footnote{13} as the possible origin of the $\beta$ relaxation in SCL. This is the only relaxation in IG in which there are no L-type particles, whereas there are many L-type particles in SCL contributing to the $\alpha$ relaxation. Hence, we can use the density $n_L$ of L-type particles as the order parameter to describe the IG transition: it is non-zero in SCL and gradually vanishes at $T_K$ as the temperature is reduced; it remains zero in the IG state. We can use the proximity of two L-type particles to determine if they are "connected" to form a cluster. These clusters can be classified as liquid-like clusters (formed by L particles). One can similarly define a solid-like cluster. Indeed, IG is a macroscopically large random solid cluster with no liquid-like clusters embedded in it. At all higher temperatures, both clusters will be continuously changing in time, but their average densities will remain constant, similar to what
happens in physical gelation.\textsuperscript{41,42,43} Therefore, we may be dealing with the phenomenon of percolation. A very similar picture has been developed by Novikov et al.\textsuperscript{44} Another picture involving two kinds of regions very similar to the above has been proposed by de Gennes.\textsuperscript{45}

Let us now turn to the lattice model. The IG forms a single macroscopic cluster of solid-like atoms, in which the density $n_L = 0$. A real glass, on the other hand, even at $T_K$, would have a non-zero $n_L$; the latter would presumably remain non-zero in a real glass even at $T = 0$, and would give rise to an additional energy to the real glass above $E_K$ and to the residual entropy at absolute zero.\textsuperscript{46} Thus, the concept of the order parameter makes sense only in the context of the ideal glass transition. We, therefore, hope that our calculation would be able to shed some light on this issue.

IV. LATTICE MODEL

A. Motivation

We have already argued in Sect. II B that the communal entropy is the central quantity of interest for the glass transition, whose vanishing locates the glass transition. The configurational contribution $S_b(T)$ due to the confinement plays no role in locating the glass transition. Accordingly, we focus our attention on only on $S_{\text{comm}}(T)$, and as remarked above in Sect. II B, we accomplish this easily by considering a lattice model in which $S_b(T) = 0$.

The simplest way to obtain the lattice is to replace each cell by a point called site, and connecting neighboring sites by bonds. The particles or voids in the system are restricted to be on these sites. The cell-site transformation results in a lattice structure in which the coordination number of each site will in general not be the same as shown by the pentagon near the top right in (a) in Figs. 1 and 2, while it will be the same in the ordered state as shown in (b) Figs. 1 and 2. If all the cells are occupied by a particle as shown in Fig. 1 then the number of sites is fixed and equal to $N$, the number of particles. The case when there are empty cells is shown in Fig. 2. In this case, the number of sites will be larger than $N$.

Let us first consider Fig. 1 for simplicity with no empty sites. The lowest energy ordered and disordered states are easy to distinguish because of the disordered lattice in (a). To
ensure this distinction will require considering a disordered lattice to describe a glass, which creates a complication as it is much easier to deal with a homogeneous lattice. This is easily taken care of by allowing voids so that the same homogeneous lattice can describe an ordered and disordered state by simply having an ordered and disordered distribution of particles and voids. Such a distinction cannot be made if there were no voids. There exists a potential energy $E$ for each distribution, and the problem reduces to knowing the multiplicity, and hence the entropy $S(E)$ of each of the possible energy $E$.

B. Antiferromagnetic Ising Model

We can use an Ising spin $S$ to represent the particle ($S = +1$) or the void ($S = -1$). One can also use the Ising spin to denote particles A and B of different species. We take $S = +1$ to denote A, and $S = -1$ to denote B particles for an alloy or a binary mixture. Thus, the model we use can either be interpreted as a compressible pure component or an incompressible binary mixture or an alloy by a slight change in the interpretation. The Ising spins are located at each site of the lattice. As voids are surrounded by particles and particles surrounded by voids in the ordered state, this staggered distribution requires an antiferromagnetic interaction between the Ising spins. We introduce the following AF Ising model in zero magnetic field on a square or a cubic lattice (lattice spacing $a$) with the interaction energy

$$E = J \sum S S' + J' \sum S S' S'', \quad J > 0.$$  \hspace{1cm} (15)

The first sum is over nearest-neighbor spin pairs and the second over neighboring spin triplets, which we take to be within a square for simplicity. The PF is given by

$$Z(T) = \sum_{\{S_{\pm 1}\}} \exp(-\beta E),$$  \hspace{1cm} (16)

where the sum is over all configurations of the $N$ Ising spin states. For $|J'| \leq 2J$, we have an AF ordering at low temperatures with a sublattice structure: spins of a given orientation are found preferentially on one of the two sublattices. Antiferromagnetically ordered squares (AFS) with spins alternating, and ferromagnetically ordered squares (FS) with spins in the same state are the only two square conformations that contribute to the first term in (15). We may identify the AF ordered structure as a crystal. For two particles of the same species, this model represents a repulsion at a lattice spacing $a$. Thus, two particles of
the same species prefer to be next-neighbor, with a particle of a different species at the intermediate site. In CR, such a situation is preferred. For a glass, three particles of the same species can occur on neighboring sites, which then raises the energy with respect to CR. Thus, the model seems to capture the correct physics to give rise to a glass.

For $|J'| \geq 2J$, the AF ordering is destroyed at low temperatures; $S$ is the same everywhere at $T = 0$. We set $J=1$ to set the temperature scale and only consider $|J'| \leq 2J$. It is easy to see that the free energy depends on $|J'|$, not on its sign. In particular, the ground state energy per spin of the AF ordered state is $E_0 = -2J$, regardless of $J'$. In the following, we will measure the energy and the free energy with respect to the ground state to give the excitation energies. In this case, both will vanish at $T = 0$. The non-zero value of $|J'|$ creates a preference for the product $SS'S''$ in a square to be of a fixed sign, which then competes with the formation of the crystal in which this product can be of either sign. A positive (negative) $J'$ provides a preference for $S = -1 (+1)$, so $J'$ can be used to also control the abundance of one of the spin states.

C. Recursive Lattice

The entropy $S(T)$ of the model cannot be negative if the state has to occur in Nature or in simulations; indeed, neither can ever produce a state, which will exhibit any entropy crisis. If the metastable state entropy $S(T) = 0$ at a positive temperature $T_K$ as the temperature is reduced, then it must stop there. Its mathematical extension to any lower temperature will necessarily give rise to an entropy crisis and must be replaced by an ideal glass below $T_K$, the ideal glass transition temperature. Thus, the partition function for the metastable state in this case makes physical sense only over $T \geq T_K$. This is accomplished by restricting the sum in (16) to disordered configurations for $E \geq E_K$

$$Z_{\text{dis}}(T) = \sum_{E \geq E_K} W_{\text{dis}}(E) \exp(-\beta E), \ W_{\text{dis}}(E_K) = 1; \quad (17)$$

see Fig. 3. The temperature $T_K$ is given by (4) applied to $S_{\text{dis}}(E)$ at $E_K$. The above PF is not physically meaningful below $T_K$, even though it can be mathematically continued to lower temperatures by considering $W_{\text{dis}}(E) < 1$ below $E_K$. As we will see, the method of calculation reported in Sect. gives the continuation of the free energy. This continuation is the origin of a negative entropy that we report in Sect. The mathematical extension
FIG. 4: A small portion of a recursive Husimi cactus with two squares ($q = 2$) meeting at each sites. The sites of the squares are labeled as shown, with the site index increasing as we move away from the origin $m = 0$.

describes a stable state in that the heat capacity remains non-negative. It only suffers from a negative entropy, something that happens in classical statistical mechanics such as for ideal gas. This issue has been discussed elsewhere by us.$^{19}$

The model cannot be solved exactly except in one dimension. It is usually studied in the mean-field approximation commonly known as the Bragg-Williams approximation$^{47}$ adapted for an AF case. However, the approximations is known to be very crude. Indeed, Netz and Berker$^{48}$ have shown that one of the shortcomings of the approximation is that it abandons the hard-spin condition $S^2 = 1$. This condition is easily incorporated in exact calculations on recursive lattices$^{49}$ and it was discovered that such calculations are more reliable than the conventional mean-field approximations. Therefore, we adopt the recursive lattice approach here.

We consider a Husimi lattice made of squares, on which the model can be solved exactly.$^{49}$ We consider the simplest lattice shown in Fig. 4 in which only two squares ($q = 2$) meet at a site; they cannot share a lattice bond. The method is easily extended to consider more than two squares ($q > 2$) meeting at a site. The squares are connected so that there are no closed loops except those formed by the squares. The lattice can be thought as
an approximation of a square lattice for \( q = 2 \) or a cubic lattice for \( q = 3 \), so that the exact Husimi lattice solution can be thought of as an approximate solution of the square lattice model or a cubic lattice, respectively. Of course, we can also think of the solution as the exact solution on a recursive lattice, although artificial. The exactness ensures that stability will always be satisfied. 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.

V. SOLUTION

The method of the solution recursively is standard by now.\[^{49}\] We label sites on the lattice by an index \( m \), which increases sequentially outwards from \( m = 0 \) at the origin; see Fig. 4. We introduce partial PF’s \( Z_m(\uparrow) \) and \( Z_m(\downarrow) \), depending on the states of the spin at the \( m \)-th lattice level, which represent the contribution of the part of the lattice above that level to the PF, subject to the condition that the spin state of the spin at the \( m \)-th lattice level is \( \uparrow \) or \( \downarrow \) respectively. We then construct recursion relations (RRs) between the partial PFs at level \( m \) in terms of the partial PFs at higher levels \( m + 1 \) and \( m + 2 \) using the standard method.\[^{49}\] We introduce the ratio

\[
x_m \equiv \frac{Z_m(\uparrow)}{[Z_m(\uparrow) + Z_m(\downarrow)]},
\]

which is found to satisfy the recursion relation

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

where

\[
f(x, x', v) \equiv x^{2r} x'^{r} / uv^2 + 2x^{r} x'^{r} y' v + x^{2r} y'^{r} v + u x^{r} y'^{r} v + 2 x'^{r} y'^{r} v + y'^{2r} y'^{-r} / v,
\]

\[
g(x, x', v) = f(x, x', v) + f(y, y', 1/v),
\]

with \( r = q - 1 \) and where

\[
u \equiv e^{4\beta}, v \equiv e^{2\beta J'}, y \equiv 1 - x, y' \equiv 1 - x'.
\]

There are two kinds of fix-point (FP) solutions of the recursion relation \(^{19}\) that describe the bulk behavior.\[^{49}\] In the 1-cycle solution, the FP solution becomes independent of the
level \( m \), and is represented by \( x^* \). It is given by

\[
x^* \equiv \frac{f(x^*, x^*, v)}{g(x^*, x^*, v)}
\]

For \( J' = 0 \), \( x^* \) is given by \( x^* = 1/2 \), as can be checked explicitly. For \( J' \neq 0 \), \( x^* \neq 1/2 \) and has to be obtained numerically. This solution exists at all temperatures \( T \geq 0 \); thus, there is no spinodal of this solution. This solution describes the disordered phase. The other FP solution of interest is a 2-cycle solution associated with the AF state containing AFSs.\(^{49}\) It alternates between two values \( x_1^* \) and \( x_2^* \) which occur at successive levels. It is given by

\[
x_1^* \equiv \frac{f(x_2^*, x_1^*, v)}{g(x_1^*, x_2^*, v)}, \quad x_2^* \equiv \frac{f(x_1^*, x_2^*, v)}{g(x_2^*, x_1^*, v)}.
\]

This kind of FP solution has also been observed in other systems such as semi-flexible polymers\(^{17,18}\), dimers\(^{19}\) and stars and dendrimers\(^{35}\) and has been thoroughly investigated. At \( T = 0 \), the 2-cycle solution is given by \( x_1^*, x_2^* = 1, 0 \) or \( 0, 1 \) describing the perfect crystal. This solution then evolves with \( T \) due to excitations and describes the crystal at low temperatures. The free energy is calculated by the general method due to Gujrati.\(^{17,35,49}\) Whichever solution has the lower free energy represents the equilibrium state. The solution with the higher free energy, then, represents SMS. Both solutions can only be observed in Nature if their entropy remains non-negative. The temperature where the two solutions have the same free energy is the transition temperature, which we denote by \( T_M \).

Let \( \phi_{FS} \) and \( \phi_{AFS} \) denote the density of squares per site in which the four spins are ferromagnetically ordered (\( \uparrow\uparrow\uparrow\uparrow \) or \( \downarrow\downarrow\downarrow\downarrow \)) and antiferromagnetically ordered (\( \uparrow\downarrow\uparrow\downarrow \)), respectively. These densities are calculated below; see (21). At \( T \to \infty \), all spins are uncorrelated so that the density per site \( \phi_{FS} = 1/16 \), and \( \phi_{AFS} = 1/16 \), and the entropy per spin is \( S = \ln 2 \). As \( T \) is reduced, \( \phi_{FS} \) decreases, while \( \phi_{AFS} \) increases. For the perfect crystal, which occurs at absolute zero, \( \phi_{FS} = 0, \phi_{AFS} = 1/2 \).

\[\text{VI. RESULTS}\]

\[\text{A. Ideal Glass transition}\]

The results for \( q = 2 \) are presented in Figs. 5,7 where all the quantities are defined as per spin (or particle). The free energy \( F_{\text{dis}} \) and entropy \( S_{\text{dis}} \) (per spin) associated with the 1-cycle FP solution are shown by the continuous and the long dash blue curves in Fig. 5.
FIG. 5: The free energy and entropy for the two FP solutions. The model shows an entropy crisis and an ideal glass transition at $T_K$. The thin curves, indicated by an asterisk, represent unphysical states below $T_K$ (negative entropy) and are replaced by the ideal glass state IG.

The free energy $F_{\text{ord}}$ and entropy $S_{\text{ord}}$ associate with the 2-cycle FP solution are shown by the continuous and the long dash red curves. The energy $E(T)$ as a function of $T$ and the entropy $S(E)$ as a function of $E$ are shown in Fig. 6. We have set $J' = 0.01$ for Figs. 5 and 6. The energy $E$ and the free energy $F$ are defined so that they represent the contributions of excitations with respect to the ground state energy $E_0 = -2J = -2$, so that they vanish at $T = 0$, as is clearly seen in Figs. 5 and 6. The transition temperature from disordered state to the ordered state is found to be $T_M \approx 2.7706$. We see from Fig. 5 that $F_{\text{dis}}$ crosses zero and becomes positive below $T = T_{eq} \approx 2.200$. This is in accordance with Fig. 3, see line OO'. The free energy $F_{\text{dis}}$ again becomes zero (not shown here, but we have checked it) as $T \to 0$; compare it with the free energy in the inset in Fig. 3. Thus, $F_{\text{dis}}$ possesses a maximum at an intermediate temperature (see point K in Fig. 5) at $T = T_K \approx 1.1316$, so that the entropy $S_{\text{dis}}$ vanishes there. Another interesting observation is that $F_{\text{dis}}(T = 0) = F_{\text{ord}}(T = 0) = 0$. We have seen this to hold in all our previous calculations also.

The calculation for the disordered metastable state in our recursive method also yields the disordered quantities below $T_K$, even though the PF in (17) is not physically meaningful because of the negative entropy. Below $T_K$, the mathematical functions $F_{\text{dis}}$ and $S_{\text{dis}}$, shown
by their thin portions in Figs. 5 and 6 in our calculation continue to satisfy the stability condition (non-negative specific heat). Despite this, they do not represent any physical states in the system due to negative entropy and have to be discarded as unphysical. Below $T_K$, we must connect the metastable state (described by $F_{\text{dis}}$ and $S_{\text{dis}}$ between $T_K$ and $T_M$) by a glassy phase of a constant free energy $F = F_{\text{IG}}$, see the green horizontal line in Fig. 5 and $S_{\text{dis}} = S_{\text{IG}} = 0$. The 1-cycle energy at $K$ is $E_{1K} = F_{\text{IG}} \simeq 0.301$. The entropy $S_{\text{ord}}$ is never negative, and the 2-cycle FP solution represents the equilibrium crystal below $T_M$. We should observe that $S_{\text{ord}} \geq S_{\text{IG}} = 0$ over $T < T_K \simeq 1.1316$. The same also holds for the Flory model of semiflexible polymers studied by our group and for anisotropic dimer model. However, it does not happen in the calculation by Gibbs and DiMarzio because of the poor approximation. The specific heat of the ordered phase is much higher than that of the disordered phase, so that the entropy of CR at low temperatures near $T_K$ is very small. We also observe that the behavior of the entropy in the ordered and disordered states in Fig. 6 is consistent with that in Fig. 3. In particular, $S_{\text{dis}}$ has a positive slope at $E_{K}$ in accordance with Fig. 3. This feature is responsible for the entropy crisis at a positive temperature $T_K$. The same is true of the behavior of the free energy in Fig. 5, which is consistent with that reported in the inset in Fig. 3. The free energy has a maximum at $T_K > 0$.

B. Competition with Crystal Ordering

The behavior as a function of $|J'|$ of the transition temperature $T_M$ (empty circles), the ideal glass transition temperature $T_K$ (filled circles) and their ratio $T_M/T_K$ (triangles) are shown in Fig. 7. As said above, $|J'|$ competes with the crystal ordering and reduces $T_M$. One can use the inverse ratio $T_K/T_M$ as a measure of the relative ease of glass formation: larger this value, easier it is to obtain the ideal glass as $T_K$ is not too deep relative to $T_M$. This relative depth is measured by the ratio $T_K/T_M$. What we observe is that $T_M/T_K$ increases with $|J'|$, with $T_K$ approaching zero faster than $T_M$, so that the ratio $T_M/T_K$ continues to increase with $|J'|$. This implies that it becomes harder to obtain the ideal glass as $T_K$ becomes relatively farther away from $T_M$ as $|J'|$ increases. The competition provided by $|J'|$ weakens not only crystal ordering but also ”weakens” forming the ideal glass. Consequently, competition does not enhance the ability to undergo ideal glass transition, an interesting
FIG. 6: \( S - E - T \) relationship for the two FP solutions. The excitations in the two solutions near \( T = 0 \) are very different. The excitations in the 1-cycle state near \( T_K \) are strongly interacting and correlated in the form of FSs as opposed to those near \( T = 0 \).

result which is being explored further\textsuperscript{50} to see if other competitions behave similarly.

We have considered a small value of \( J' \) in order to compare the results with the simple case \( J' = 0 \), which is analytically solvable; see Sect. VI C. The complete analysis for other values of \( J' \) will be reported later\textsuperscript{51}. Here, we quote the results for a larger value of \( J' = 1.6 \). The melting temperature \( T_M \approx 1.762 \), see Fig. \ref{fig:7}, where \( S_{\text{dis}} \approx 0.40999 \) and \( S_{\text{ord}} \approx 0.40947 \), and the shifted free energy is \( F \approx -0.299026 \). The ideal glass occurs at \( T_K \approx 0.377 \), as shown in Fig. \ref{fig:7}. We notice that the entropy discontinuity is not very large at \( T_M \); however, the entropy of the ordered phase drops very fast just below \( T_M \) so that around \( T_K \), the CR entropy is quite small (result not shown); compare with Fig. \ref{fig:5} where the drop is similarly fast.
FIG. 7: The effect of $|J'|$, which creates competition with the crystal ordering, on $T_M$ and $T_K$ and their ratio. The weakening of crystal ordering also "weakens" the ideal glass formation.

C. Analysis of Defects

1. Disordered Phase

To understand the difference between the defects in the disordered liquid and the crystal, we turn to Fig. 6 and observe that near $T = 0$, the excitation energies of both FP solutions are very different, even though $E_{\text{dis}}(0) = E_{\text{ord}}(0) = 0$. Detailed analysis will be presented elsewhere. The excitations (defects) in the crystal are known to be due to point-like excitations caused by the reversal of a single spin which changes the free energy by $\simeq 8J$ (coordination number 4) with respect to the ground state; here we assume $J'$ to be small. Therefore, this excitation causes the leading term in the free energy $F_{\text{ord}}$ to be $1/u^2$ and can be treated as non-interacting as long as they are small in number. The exact recursive method also allows us to calculate the densities of various excitations and defects. In particular, the densities $\phi_{\text{FS}}$ and $\phi_{\text{AFS}}$ are easy to calculate. For the 2-cycle solution $(x_1^*, x_2^*, x_1^*, x_2^*, \ldots)$, they are given by

$$
\phi_{\text{FS}} = \frac{x_1^{2r} x_2^{2r} / v^2 + y_1^{2r} y_2^{2r} v^2}{2ug(x_1^*, x_2^*, v)(x_1^{eq} + y_1^{eq})}, \quad \phi_{\text{AFS}} = \frac{[x_1^{2r} y_2^{2r} + y_1^{2r} x_2^{2r}]u}{2g(x_1^*, x_2^*, v)(x_1^{eq} + y_1^{eq})}, \quad \alpha = 1, 2.
$$

(21)
The densities per site of up (↑) and down (↓) spins are given by

\[ \phi_{\text{up}} = \frac{x^{aq}_\alpha}{x^{aq}_\alpha + y^{aq}_\alpha}, \quad \phi_{\text{down}} = \frac{y^{aq}_\alpha}{x^{aq}_\alpha + y^{aq}_\alpha}, \quad \alpha = 1, 2. \] (22)

By setting \( x^{*}_1 = x^{*}_2 = x^* \), the same expressions will also give the values of \( \phi_{\text{FS}} \) and \( \phi_{\text{AFS}} \) or \( \phi_{\text{up}} \) and \( \phi_{\text{down}} \) for the disordered state.

What kinds of excitations are deducible from the form of \( F_{\text{dis}} \) near \( T = T_K \)? To answer this, we consider the simple case of \( J' = 0 \). In this case, the 1-cycle solution is given by \( x^* = 1/2 \) at all temperatures. This solution also gives us \( F_{\text{dis}} \) over the entire temperature range (physical and unphysical) \( T \geq 0 \). As we are only interested in the excitation energy, we have shifted the free energy so that it vanishes at \( T = 0 \). The unphysical nature of this free energy (negative entropy) between \( T = 0 \) and \( T = T_K \) does not affect the energy as the specific heat is non-negative; it only affects the entropy. This portion of the free energy will correctly give the information about the energy and the nature of excitations at \( T_K \) or above. From now on, we consider \( r = 1 \). The shifted free energy is given by

\[ F_{\text{dis}}(T) = -(T/2) \ln w + 2, \]

where we have introduced

\[ w = 3 + u/2 + 1/2u = 4g(1/2, 1/2, 1), \]

where \( g(1/2, 1/2, 1) \) is the value of \( g(x, x', v) \) in (20b) at the 1-cycle fix-point for \( v = 1 \). The excitation energy is obtained from the free energy, and is given by

\[ E_{\text{dis}}(T) = -(u - 1/u)/w + 2, \]

which can be written as

\[ E_{\text{dis}}(T) = 4(\phi_{\text{FS}} - \phi_{\text{AFS}}) + 2, \]

in terms of \( \phi_{\text{FS}} \) and \( \phi_{\text{AFS}} \), which from (21) are given by

\[ \phi_{\text{FS}} = 1/4uw, \quad \phi_{\text{AFS}} = u/4w \]

for the 1-cycle solution. The entropy is calculated using

\[ S_{\text{dis}}(T) = (E_{\text{dis}} - F_{\text{dis}})/T. \]
The densities of up and down spins are equal at all temperatures

$$\phi_{\text{up}} = \phi_{\text{down}} = 1/2.$$  

Thus, the disordered state corresponds equal number of up and down spins at all $T \geq 0$. At $T = 0$, $E_{\text{dis}}(0) = 0$, which implies that all squares are AFS. Thus, as the temperature is raised, more and more FS’s appear by changing a AFS into a FS. Near $T = 0$, we find that

$$E_{\text{dis}}(T) \simeq 12/u,$$

$$F_{\text{dis}}(T) \simeq T\left(\frac{1}{2}\ln 2 - 3/u\right),$$

$$S_{\text{dis}}(T) \simeq -\frac{1}{2}\ln 2 + 3/u + 12\beta/u.$$  

At $T = 0$, $S_{\text{dis}}(0)$ in Fig. 5 is found to be almost $-\frac{1}{2}\ln 2$. What we discover is that the excitations due to $1/u$-term near $T = 0$ are not the *uncorrelated* single spin reversal in the background of a perfect crystal; the latter require an excitation energy of $8J$ and a correction of order $1/u^2$ in the free energy of the ordered state. Rather, they represent *correlated* excitations in the form of FS in the background of AFSs by turning an AFS into a FS. Each FS excitation requires an energy $4J$ per site. This is in accordance with the general discussion above. Indeed, the excitation spectrum is given by the expansion of $E_{\text{dis}}(T)$ in powers of $1/u$. These excitations also explain why the thin portion of $E_{\text{dis}}(T)$ rises more rapidly than $E_{\text{ord}}(T)$ in Fig. 4 so that $E_{K} \simeq 0.3$ is appreciably higher than the $E_{\text{ord}}(T) \simeq 0.1$ at $T_{K}$ due to a lower $\phi_{\text{AFS}}$ and higher $\phi_{\text{FS}} \simeq 3.58 \times 10^{-4}$ in the metastable state

$$\phi_{\text{AFS}} \simeq 0.426, \ \phi_{\text{FS}} \simeq 3.58 \times 10^{-4},$$

relative to

$$\phi_{\text{AFS}} \simeq 0.498, \ \phi_{\text{FS}} \simeq 7.991 \times 10^{-7}$$

in the crystal. The density of sites

$$\phi_{\text{unc}} \equiv 1 - 2(\phi_{\text{FS}} + \phi_{\text{AFS}})$$

not covered by AFSs and FS’s is

$$\phi_{\text{unc}} \simeq 0.148 \text{ in SCL},$$

$$\phi_{\text{unc}} \simeq 3.684 \times 10^{-3} \text{ in CR}.$$
These sites are probably uncorrelated in CR to account for non-zero entropy of CR at $T_K$, but this needs to be carefully checked. However, these sites and the two kinds of squares must be strongly correlated in SCL and IG at $T_K$ to ensure that the entropy is zero.

2. Ordered Phase

The CR entropy $S_{\text{ord}}(T)$ vanishes only at absolute zero, but remains non-zero at any other temperature. This is consistent with defects in the crystal near $T = 0$ being point defects. As the lattice entropy represents the communal entropy, it is not zero for CR. As a consequence, CR is not confined to a single basin, as required by [8], due to the presence of point defects that emerge in the ideal CR. The presence of point defects gives rise to basins different from the basin corresponding to the perfect CR at absolute zero. In a real CR, there will be additional contribution $S_b(T)$ due to vibrations inside these basins. The point defects form a dilute system near $T = 0$, so that there is practically no correlation among them. Thus, as discussed earlier in Sect. III B, the derivative in (4) is infinitely large for the perfect CR.

D. Nature of the Ideal Glass

As there is no non-analyticity in the computed (physical and unphysical) $F_{\text{dis}}(T)$ of SCL at $T_K$, the excitation spectrum remains continuous at $T_K$. Thus, it can be continued above $T_K$ where physical states (non-negative entropies) occur. The above analysis leads us to conclude that the excitations at or above $T_K$ in SCL are very different from the point defects of the crystal and are the ones that get frozen in the ideal glass that is formed at $T_K$. For $T < T_K$, we have an ideal glass, shown by the horizontal short dash curve in Fig. 6 of constant energy $E_K$ and zero entropy. Let us try to understand how the entropy of a disordered state can be zero. Let us consider a system consisting of $N$ Ising spins. Let $W_{\text{dis}}$ denote the number of disordered microstates, which we index by $i = 1, 2, \cdots, W_{\text{dis}}$. Let $E_i$ denote the energy (and not the energy per site) of the $i$th microstate, and $p_i$ its probability to occur. The latter is given by

$$p_i = e^{\beta(N F_{\text{dis}} - E_i)}$, \quad (\sum p_i = 1),$$
and the entropy per spin $S_{\text{dis}}$ is given by

$$NS_{\text{dis}} = - \sum_{i=1,W_{\text{dis}}} p_i \ln p_i.$$  

The entropy can be zero\textsuperscript{22} if and only if one of the probabilities is unity, while all other probabilities are zero. Let $i = i_0$ denote the particular disordered microstate for which

$$p_{i_0} = 1.$$  

This particular disordered microstate, being the only one of energy $E_{i_0}$, also represents the \textit{macrostate} identified as the ideal glass at $T \leq T_K$. The energy of this microstate per spin is

$$E_{i_0}/N \equiv E_K \equiv F_{\text{IG}}.$$  

This discussion clearly shows how the entropy of IG can be less than that of the CR at the same temperature $T \leq T_K$. There is nothing paradoxical here. The analysis also shows that the microstate $i_0$ emerges out of the above defects frozen at $T_K$. These defects also determine the nature of solid-like clusters discussed in Sect. III C that survive at $T_K$. These clusters pack the lattice in a \textit{unique} way to generate the microstate $i_0$, so that the resulting entropy vanishes. From what has been said above, these clusters are strongly correlated. How this correlation comes about as SCL approaches $T_K$ is something we are not able to answer at present and is under investigation. Understanding the nature of this unique microstate is certainly a challenging problem in theoretical physics at present.

\textbf{E. Excitation Spectra in Real Glasses}

The excitation spectra of both solutions over the physical range are completely described by their respective entropies $S_{\text{dis}}(E)$ (the thick part) and $S_{\text{ord}}(E)$ shown in Fig. 6. For $E < E_K$, the excitations in IG cannot change since they are frozen at constant energy $E_K$ into the unique microstate $i_0$, but continue to change in the crystal. In experiments, the ideal glass will never be observed due to time-limitations and one would obtain a non-stationary state, see the green curve GF in Fig. 3 whose entropy $S_{\text{NEQS}}(E)$ must satisfy $S_{\text{NEQS}}(E) \leq S_{\text{dis}}(E)$ according to the law of increase of entropy.\textsuperscript{23} It can be shown\textsuperscript{11} that at a given temperature, the energy and entropy of the a NEQS continue to decrease in time as the state approaches SMS. Thus, the non-stationary glass will have some extra excitations

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at low temperatures with respect to the IG at that temperature. These defects are the one that we have associated with $n_L$ in Sect. III C. The excitations just above $T_K$ as IG "melts" into SCL are also due to the liquid-like clusters introduced in Sect. III C which must be strongly correlated. The associated excitation energy of these clusters is given by the behavior of $E_{\text{dis}}(T)$ above $T_K$.

The down spins (voids) distribute themselves in the lattice at equilibrium, and the corresponding 1-cycle solution gives rise to an excitation spectrum so that $S_{\text{dis}}(E)$ vanishes at $T_K$. If it happens that the system is quenched, then all we can say is that the corresponding spectrum $	ilde{S}_{\text{dis}}(E)$ of the quenched system, which should be similar to the green curve GF in Fig. 3, must satisfy the standard condition $\tilde{S}_1(E) \leq S_1(E)$. Despite this, the entropy of the quenched system does not vanish at a positive temperature.11 There is no contradiction.

F. Ferromagnetic Case

For the AF case that we consider here, the 1-cycle solution is found to exist at all temperatures and describes the disordered liquid above and its metastable continuation below the transition temperature. There is no singularity in this fix-point solution at the transition. In contrast, for the ferromagnetic case ($J < 0$), the 2-cycle FP solution is never stable, and the 1-cycle solution has a singularity at the ferromagnetic transition and its entropy never becomes negative. This is not surprising as the ferromagnetic Ising model is suitable to describe liquid-gas transition which is known to have a critical point. Thus, this model is not suitable to study supercooling.

VII. SUMMARY

To summarize, our model calculation demonstrates that monatomic systems also give rise to an ideal glass and an energy gap. This was one of our two goals and, in conjunction with the earlier work of Gibbs and DiMarzio15 and from our group17,18 for long polymers and for anisotropic dimer model19,20 strongly suggests that the entropy crisis is ubiquitous in molecules of all sizes. The other goal was to learn about generic properties of ideal glasses such as the nature of defects. To this end, we have verified that our proposed energy gap model in Sect. III, which is consistent with our previous exact calculations9,10,16,17,18,19,20,23.
is also consistent with our current model calculation of monatomic glass formers. The macrostate associated with the ideal glass contains only one microstate because its entropy is zero. This fact makes defects in IG to be highly correlated so that the energy of excitation and the resulting entropy are proportional to each other; see (10) and (13). The constant of proportionality is $T_K$. Thus, the strongly correlated defects in glass at $T_K$ are very different from those in the crystal, in which they are mostly uncorrelated near $T = 0$. Because of the strong correlation, the defects in IG cannot be removed to lower its energy and still leave the microstate disordered. Of course, one can remove a lot of defects to bring its energy to that of CR at any temperature below $T_K$, but this will convert IG to an ordered state. The energy required to do so will be extensive and its probability will be almost zero at such temperatures.

The defects in real glasses will be local, as discussed in Sect. III B. Accordingly, one can have a real glass approach absolute zero, where its entropy need not vanish. As the glass relaxes, its entropy and free energy will continue to decrease as shown elsewhere. Eventually, its entropy will vanish. During relaxation, the size of the defects will continuously grow until they become non-local. The time required to completely relax is probably so long compared to experimental time scales that a real glass will never completely relax.

The existence of the gap is used to prove that IG in SCL that emerges in any generic system must appear at a positive and finite temperature $T_K$, which is seen in all exact recursive lattice calculations from our group, and the exact calculation in a one-dimensional polymeric system. The proof presented in this work is more direct and simple compared to an earlier proof, which was somewhat involved.

We use the relative depth of $T_K$ below the melting temperature $T_M$ as a measure of ease of forming a glass. A smaller value of this ratio is taken to imply that it is more easy to form a glass, as one does not have to supercool too much below the melting temperature $T_M$. The ratio is related to the relative depth $(T_M - T_K)/T_M$. Our model calculation shows that the competition does not necessarily enhance the ability to form a glass.

We have been unable to completely specify the actual IG microstate, except to note that its energy cannot be reduced by removing some of its defects and that its defects cannot be interchanged because that will generate another microstate, different from IG. The latter will violate the uniqueness of IG (zero entropy). However, it would be desirable to obtain more specific information about this unique microstate. It remains a challenge in theoretical
physics to even decide how such a disordered microstate should be characterized. The work we have reported uses a classical model. It would be interesting to see if a similar calculation can be carried out for a quantum system in which configurational degrees of freedom cannot be separated from the kinetic degrees of freedom. Such a separation was required for the introduction of the communal entropy. A quantum model calculation will clarify if the communal entropy can still be defined and if it has any relevance for IG.

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$$f_A(x) = Ax^{2n} \exp(-1/x^2), \ A, n \text{ are constants},$$

which is singular at $x = 0$, but exists on both sides of the singularity. Of course, one can patch two functions at $x = 0$ with different $A$ for either sides of $x = 0$ to construct an infinite number of functions, but this is irrelevant for the existence of $f_A(x)$. In principle, any thermodynamic function is uniquely obtained by taking the thermodynamic limit. For example, the above function can emerge from

$$f_{A,N}(x) = Ax^{2n} \exp[-1/(x^2 + \alpha/N^m)],$$

as $N \to \infty$ ($m > 0; \alpha$ a constant), and is uniquely defined on both sides of $x = 0$.  

35
The two coexisting phases in liquid-gas transitions have identical symmetry in that they are simply related by a symmetry operation like the up-down symmetry in the Ising model. No symmetry operation can transform crystals into liquids, and vice versa.

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28 It should be emphasized that the way it has been introduced, \( W(E,V)dE/\varepsilon_0 \) does not either have to be an integer or unique because of the introduction of \( v_0 \) and \( \varepsilon_0 \). This is a common problem in classical statistical mechanics and one must go a quantum description to make the number of microstates to be an integer and unique. Despite this, the communal entropy in (5) is expected to be non-negative even in classical thermodynamics if it is associated with the number of basins or with deconfinement; see Sect. III

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(Sect. 64)

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