Relevance of the Inherent Structures and Related Fundamental Assumptions in the Energy Landscape

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Abstract

We carefully investigate the two fundamental assumptions in the Stillinger-Weber analysis of the inherent structures (IS’s) in the energy landscape and come to conclude that they cannot be validated. This explains some of the conflicting results between their conclusions and some recent rigorous and exact results. Our analysis shows that basin free energies, and not IS’s, are useful for understanding glasses.

It is well known that most supercooled liquids (SCL) become viscous when their configurational entropy \( S(T) \) becomes negligible as they are cooled, provided the corresponding crystal (CR) is not allowed to nucleate. The flow practically ceases over a period constrained by experimental limits, the viscosity becomes very large, and the viscous fluid eventually becomes an amorphous solid or glass. Our current understanding of glassy behavior is still far from complete, even after many decades of continuous investigation. In order to better understand the flow properties of viscous fluids, Goldstein proposed the potential energy landscape picture using classical statistical mechanical canonical ensemble \[2\], in which the energy barriers control the flow at low temperatures. The discussion was mostly qualitative, but provided an interesting and sufficiently tractable scheme and included some quantitative predictions in the SCL and the glassy states. Stillinger and Weber (SW) later revived this picture, carried out an analysis in terms of basins, and concluded that their minima, called the inherent structures (IS), play a pivotal role in the thermodynamics of viscous fluids at low temperatures \[3, 4\]. The IS-entropy \( S_{IS}(T) \) [not to be confused with \( S(T) \)] of the IS’s vanishes at some \( T = T_{SW} \) (called \( T_K \) by SW), but we will reserve \( T_K \) where \( S(T) = 0 \) \[1\] so that the system gets trapped into a single basin at \( T_{SW} \) so that \( S(T) \) becomes the basin configurational entropy \( S_b(T) \geq 0 \) below \( T_{SW} \geq T_K \) \[1\]. The SW analysis has given rise to a considerable amount of literature in recent years; for a partial list, see \[5\].
One of the most tantalizing consequences of the SW analysis is the theoretical conclusion \( T_{SW} = 0 \) drawn by Stillinger\[4\]. Consequently, it is not possible to have a configurational entropy crisis \( (S(T) < 0) \) below a positive temperature \( T_K \[1\] \) for SCL. For CR, the claim implies that just above \( T_{SW} = 0 \), CR probes many basins \( (S_{IS} > 0) \), not all of which have to be close in the configuration space, and its heat capacity is not due to pure vibrations within a single basin. This is hard to understand in view of the tremendous success of the Debye model. Stillinger’s argument also does not permit any SCL spinodal at a positive temperature. However, the latter has been observed in exact calculations for finite-length polymers \[6\] and in a binary mixture \[7\]. The theoretical conclusion \( T_{SW} = 0 \[4\] \) is contradicted by numerous numerical evidence \[5\] of a positive \( T_{SW} \) within the IS picture. A recent rigorous statistical mechanical proof by Gujrati \[8\] also contradicts this claim. He has shown that under the assumption that the ideal glass has a higher energy \( (E = E_K) \) than the corresponding crystal \( (E = E_0 < E_K) \) at absolute zero, \( S(T) \) of the stationary SCL (obtained under infinitely slow cooling of the disordered equilibrium liquid EL) must necessarily vanish at \( T_K > 0 \). At \( T_K \), SCL has its configurational energy \( E_K \). Two independent proofs are given \[8\], and the conclusions are also substantiated by two exact model calculations, one of which is not mean-field. Other exact calculations for the abstract random energy model \[9\], and for long polymers \[10\] also support the conclusions by Gujrati. In addition, a recent exact solution by Semerianov and Gujrati\[11\] of a dimer model, a prototype model of molecular liquids, also exhibits configurational entropy crisis in its stationary metastable state below a positive temperature. Corsi \[12\] has also observed positive Kauzmann temperatures in exact calculations for small particles occupying four and five lattice sites each. The important point to note is that none of these exact calculations utilizes the energy landscape. However, if the latter has any validity, its consequences must be in accordance with the exact calculations and the rigorous analysis, which is certainly not the case. Thus, we need to reexamine the SW analysis to clarify the conflict. We also provide an alternative analysis of the landscape, which is consistent with the rigorous analysis.

The canonical ensemble free energy \( F_{\text{dis}}(T) \) of the disordered EL is continued analytically \[8\] below the melting temperature \( T_M \) to give the SCL free energy. As a mathematical continuation, the resulting SCL does not have to satisfy the reality condition \( S(T) \geq 0 \). The continuation, in principle, can stop in a spinodal singularity at a positive temperature \[6\[7\]. Here, we are only interested in the case when the SCL free energy can be mathematically continued all the way down to \( T = 0 \) without encountering any singularity. It is easy to show \[8\] that, at \( T = 0 \), the SCL and CR free energies are identical \( (F = E_0) \), provided \( TS(T) \to 0 \). They are again equal at \( T_M \) because of which SCL is forced to exhibit the entropy crisis \( (S(T) < 0) \[8\] \) below \( T_K > 0 \[6\] \[8\] \[10\], where it is discarded and replaced by an ideal glass phase to satisfy the reality condition. The ideal glass has \( E = E_K \) for \( T \leq T_K \). At \( T = 0 \), the configuration corresponding to \( E_K \) must represent a potential energy minimum, provided we neglect surface effects. At a positive temperature \( T_S > T_K \), SCL gets confined
into the basin whose IS is at $E_K$. Thermal fluctuations will still allow SCL to visit other basins, which are rare if $T$ is small. We will not investigate fluctuations and restrict ourselves only to the average behavior here.

The following two observations are going to be relevant below.

G1. The zero of the temperature scale is set by the global potential energy minimum $E_0$.

G2. The ideal glass configuration at $E_K$ is a local minimum of the potential energy (neglecting surface effects), which SCL approaches at $T_K > 0$. Since SCL does not physically exist below $T_K$ (due to negative entropy), the ideal glass is put in by hand for $T < T_K$ to avoid the entropy crisis. It does not emerge directly in the statistical mechanical description.

In continuum classical statistical mechanics, the dimensionless total partition function ( PF) $Z_T$ of a system of $N$ identical particles $i = 1, 2, ..., N$ in a given volume $V$, with the Hamiltonian $E_T(\{\mathbf{r}_i, \mathbf{p}_i\}) \equiv K(\{\mathbf{p}_i\}) + E(\{\mathbf{r}_i\})$, $K, E$ being the kinetic and the configurational (i.e., the potential) energy, is a product of two independent integrals

\[ Z_T \equiv \frac{1}{(2\pi\hbar)^3N} \int e^{-\beta KE d^N\{p\}} \int e^{-\beta V d^N\{r\}}. \]  

(1)

Here $d^N\{p\}, d^N\{r\}$ represent integrations with respect to momenta and positions $\mathbf{p}_i, \mathbf{r}_i$ of the particles, and $\beta$ the inverse temperature $1/T$ in the units of the Boltzmann constant $k_B$. The second integral (the prime implying integration over distinct configurations of the particles) is called the configurational PF, to be denoted by $Z$.

The momentum integration in $Z_T$ can be expressed in terms of $W_{KE}(P)dP \equiv C_{3N}d^{3N-1}P^3/(\pi^N)$ related to the $3N$-dimensional momentum space volume within the spherical shells of radii $P$, and $P + dP$ [$C_d \equiv d^{d/2}/\Gamma(d/2 + 1)$]. The translational entropy due to the translational degrees of freedom is given by

\[ S_K(T) = \ln W_{KE}(\overline{P}), \overline{P} = \overline{P}^2/2m = 3NT/2. \]

In the thermodynamic limit $N \to \infty$, we find that $S_K(T) = (3N/2)[1 + \ln T + \ln(2\pi m/\hbar^2)]$, and has the same value at a given temperature for all classical systems, regardless of their configurational energy. Thus, in general, the entropy due to the configurational degrees of freedom can be always obtained by subtracting $S_K(T)$ from $S(T) \equiv S_T(T) - S_K(T)$, where $S_T(T)$ is the total entropy in the canonical ensemble; see (1).

For an ideal gas, $Z = V^N/N!$, so that $S = N\ln(Ve/N)$, which no longer depends on $T$. For $T < eh^2/2\pi m$, $S_K(T) < 0$, or for $V/N < 1/e$, $S(T) < 0$.

The problem of negative entropy is well known in classical statistical mechanics, and requires quantum statistical mechanics for its resolution. Unfortunately, it is not possible to solve a quantum statistical mechanical model exactly at present. Thus, care must be exercised when drawing conclusions based on the sign of the entropy. Since $T_K$ is signaled by a negative entropy, it is crucial to have a formalism in which the entropy is never negative for realizable states in Nature. The simplest way to achieve this is to discretize either
the phase space by using cells of size $h^{3N}$ or the real space by using a lattice. Thus, in the following, we take it for granted that such a discretization has been carried out. We closely follow [4] who factors out the kinetic energy part and only uses $Z$ to introduce the potential landscape picture [4, 8], and consider only the configurational entropy $S(T)$ [4], the canonical PF $Z(T)$, and the configurational free energy is $F(T) = -T \ln Z(T)$ in the following. We rewrite $Z(T)$ as follows. Let $W(E) \geq 1$ (so that $S(E) \equiv \ln W(E) \geq 0$ [8] for physically realizable states) denote the number of the configurations of potential energy $E$. Then $Z(T)$ can be rewritten as a sum over $E: Z(T) \equiv \sum_{E} e^{-\beta E W(E)}$. Replacing $W(E)$ in $Z(T)$ by the number of disordered configurations $W_{\text{dis}}(E)$, we obtain the PF $Z_{\text{dis}}(T)$ so that $F_{\text{dis}}(T) \equiv -T \ln Z_{\text{dis}}(T)$ is the free energy of the disordered phase EL and its extension SCL [3, 4, 8]. In the following, we will use $Z(T)$ to represent both PF’s, which should cause no confusion since the context will be clear.

**SW Picture.** The potential energy landscape is a union of disjoint basins. A basin is indexed by $j$, and characterized by its minimum and maximum energies $E_j$ and $E_{j,\max}$ so that it does not exist outside this energy range $\Delta_j E = (E_j, E_{j,\max})$. Let $W_j(E)$ ($E \in \Delta_j E$) represent the number of distinct states of energy $E$ in the $j$-th basin. We introduce the shifted PF

$$z_j(T) \equiv \sum_{E} W_j(E)e^{-\beta(E-E_j)} \delta_{E,\Delta_j E}$$

of the $j$-th basin. Here, $\delta_{E,\Delta_j E} = 1$ if $E \in \Delta_j E$, and 0 if $E \notin \Delta_j E$. We group basins, indexed by $j(\lambda)$, into inherent structure classes (ISC) $I_\lambda$, indexed by $\lambda$, so that all IS’s in a class have the same energy $E = E_\lambda$. The basin in a class do not have to be close in the configuration space. Let $N_{IS}(E_\lambda)$ be the number of basins in $I_\lambda$, and $S_{IS}(E_\lambda) \equiv \ln N_{IS}(E_\lambda)$. Let $Z_\lambda \equiv \sum_{j(\lambda)} z_j(T)$ and $z_\lambda \equiv Z_\lambda/N_{IS}(E_\lambda)$ denote the shifted and the average shifted $I_\lambda$-PF, so that

$$Z(T) \equiv \sum_\lambda e^{-\beta E_\lambda} Z_\lambda \equiv \sum_\lambda e^{-\beta E_\lambda + S_{IS}(E_\lambda)} z_\lambda.$$

Stillinger and Weber [3, 4] and various authors in [1] assume that $z_\lambda$ is an explicit function of $E_\lambda$, and $T$ of the form [SW denote quantities that are specific to the SW-approach]

$$z_\lambda^{(SW)}(E_\lambda, T) \equiv e^{-\beta f^{(SW)}(E_\lambda, T)}.$$

They also replace the first sum over the discrete index $\lambda$ in [3] by a sum over the almost continuous variable $E_\lambda$ so that a general summand can be characterized by $E_\lambda$ using $F^{(SW)}(E_\lambda, T) \equiv E_\lambda + f^{(SW)}(E_\lambda, T) - T S_{IS}(E_\lambda)$, whose minimum with respect to $E_\lambda$ at fixed $T$ determines $Z(T)$ for a macroscopic system. This minimum term corresponds to that particular value $E_\lambda = F_\lambda$ at which

$$\left(\partial S_{IS}(E_\lambda) / \partial E_\lambda\right)_F = \beta \left[1 + \left(\partial f^{(SW)}(E_\lambda, T) / \partial E_\lambda\right)_F\right].$$

The equilibrium free energy, and the IS-entropy are given by $F^{(SW)}(T) \equiv F^{(SW)}(E_\lambda, T)$, and $S_{IS}^{(SW)}(T) \equiv S_{IS}(E_\lambda)$, respectively. We expect $S_{IS}^{(SW)}(T)$
to vanish at some low $T = T_{SW}$ and increase monotonically with $T$ at least at low $T$. For $T \leq T_{SW}$, the system is trapped in a single basin of energy minimum $E_\lambda = E_K$ for SCL ($E_0$ for CR) so that at or below $T_{SW}$, $E_\lambda$ sticks at $E_K$ for SCL ($E_0$ for CR). Stillinger has argued that satisfying below $T_{SW}$ is inconsistent with $E_\lambda$ sticking at either $E_K$ (or $E_0$). Thus, he concludes that $T_{SW} = 0$, a consequence of which is the observation that there cannot be a positive $T_K$. This conclusion is based on the following two fundamental assumptions in the SW approach:

SW1: The shifted ISC free energy $f^{(SW)}(E_\lambda, T) - T S_{IS}(E_\lambda)$ is an explicit function of $E_\lambda$, so that the summation over $\lambda$ can be replaced by that over $E_\lambda$.

SW2: The minimization condition also holds below $T_{SW}$, where $f^{(SW)} = \delta$.

We now demonstrate that neither assumption can be substantiated.

**Current Analysis.** We observe that $W(E)$ is a sum over various basins: $W(E) \equiv \sum_j W_j(E) \delta_E \Delta_j E$. We group all basins having the same minimum at $E = E_\lambda$ together into $\mathcal{I}_\lambda$. It should be noted that $z_j(T)$ of all basins in $\mathcal{I}_\lambda$ need not be the identical in value.

1. **Evaluating $z_j(T)$**. We now prove that $z_j$ cannot depend explicitly on the basin energy minimum $E_j$, see (2), though it most certainly depends on the shape of the basin, i.e. on $j$. For example, the curvature of the basin at its minimum and not its value of $E_j$ determines the vibrational frequencies and the free energy $f_j(T) \equiv -T \ln z_j$ in the harmonic approximation. The latter is measured with respect to $E_j$, so is independent of $E_j$. To be sure, let us shift all energies $E \rightarrow E' \equiv E - C$ by some constant $C$ in (2). The number $W_j(E)$ of states, all having the same energy $E$, remains unchanged under the shift by $C$. Thus, $W_j(E) \rightarrow W'_j(E') = W_j(E)$. Thus, $z_j$ transforms under the shift as $z_j(T) \rightarrow \sum_{E'} W'_j(E') e^{-\beta(E' - E_j)} \delta_{E', \Delta_j E'}$ for any arbitrary $C$. Comparing with (2), we conclude that $z_j$ has not changed. Consequently, it does not depend on the shift $C$, including $C = E_j$.

Since $W_j(E) \geq 1$, $z_j(T)$ is a sum of positive terms. Hence, for a macroscopic system, $z_j$ is determined by the maximum summand in (2) corresponding to $E = E_j \in \Delta_j E$, and the corresponding heat capacity is non-negative. (Both observations remain valid even if $W_j(E) \geq 0$, a common occurrence in SCL continuation.)

For $E = E_j$, we have

$$\frac{\partial S_j(E)/\partial E}{\frac{\partial T}{\partial E}} = \beta, \quad E_j \in \Delta_j E \text{ or } T \in \Delta_j T,$$

where $\Delta_j T$ is the temperature range ($T_j$, $T_{j,\text{max}}$), so that the equilibrium energy $E_j(T)$ for the basin lies in the range $\Delta_j E$. According to G2, $T_j$ is strictly positive for $E_j = E_K > E_0$. Thus, we assert that $T_j$ is not necessarily zero. The basin free energy is

$$f_j(T) \equiv -T \ln z_j = \overline{E}_j - E_j - T S_j(\overline{E}_j), \quad T \in \Delta_j T.$$
The energy landscape is topologically very complex, with various basins very different from each other, even if they have their minima at the same energy. Thus, \( E_j(T) \) in different basins at the same temperature \( T \) (provided \( T \in \Delta_j \)) for these basins will be usually different. There is no requirement that they be the same. Moreover, even if the free energies \( f_j(T) \) of two or more basins happen to be the same at some temperature \( T \), they need not remain equal at other temperatures.

2. **Evaluating** \( Z_\lambda(T) \). The proper form or the ISC PF’s \( Z_\lambda(T) \) or \( z_\lambda \) in \( I_\lambda \), see (8), is

\[
Z_\lambda \equiv z_\lambda e^{S_{\text{IS}}(E_\lambda)} = \sum_{j \in \lambda} z_j \delta_{T,\Delta_j,T}.
\]

Due to the delta term, similar in definition to \( \delta_{E,\Delta_j,E} \), the sum in (8) contains only those basins in \( I_\lambda \) that exist at \( T \) in the sense that its range contains \( T : \Delta_j,T \ni T \). From now onward, we only consider those basins that exist in this sense; hence, we will not explicitly exhibit the delta term anymore. We now classify each existing basin in (8) according to its free energy \( f \). Let \( N_\lambda(f) \) denote the number of basins of free energy \( f \) that exist at a given \( T \) in \( I_\lambda \). Since \( f \) is a function of \( T \), \( S_\lambda(f) \equiv \ln N_\lambda(f) \) also changes with \( T \). For a macroscopic system at a given fixed \( T \), \( Z_\lambda \) is dominated by the basins in \( I_\lambda \) for which \( F_\lambda(f,T) \equiv f - T S_\lambda \) is minimum as a function of \( f \) at fixed \( T \). The resulting entropy and the free energy at the minimum (\( f = f_\lambda \)) are denoted by \( S_\lambda(T) = S_\lambda(f_\lambda) \), and \( F_\lambda(T) = f_\lambda - T S_\lambda \), respectively, where \( f_\lambda \) is determined by

\[
(\partial S_\lambda/\partial f)_{T_\lambda} = \beta, \ T \geq T_{S_\lambda}^{(\lambda)}.
\]

which looks similar to (6) but very different from (5). Here, \( T_{S_\lambda}^{(\lambda)} \) is the temperature at which \( S_\lambda = 0 \), so that only one basin exists below it (and above its lowest temperature \( T_j \)) in the above sense. Because of this, the issue of \( F_\lambda \)-minimization for \( T < T_{S_\lambda}^{(\lambda)} \) does not arise as there is only one member in \( I_\lambda \) (\( S_\lambda = 0 \)), so that \( F_\lambda \to f_\lambda \); thus, the minimization of \( F_\lambda \) is already ensured by (6). We should contrast (9) with (6). Stillinger puts no restriction on the applicable temperature range in the latter; see SW2. However, it is clear from our discussion that (9) cannot apply below \( T_{SW} \), which invalidates the second fundamental assumption SW2. Consequently, Stillinger’s argument that \( T_{SW} = 0 \) has no validity.

3. **Evaluating** \( Z(T) \). Using the evaluated \( Z_\lambda \) in \( Z \), we find

\[
Z = \sum_\lambda e^{-\beta [E_\lambda + F_\lambda(T)]}.
\]

We now make the following important observation. As shown above, \( f_\lambda \) is independent of \( E_\lambda \); thus, \( S_\lambda(T) \) and \( F_\lambda(T) \) are independent of \( E_\lambda \), although they most certainly depend on the ISC \( I_\lambda \). There are various aspects of the basins such as the IS-curvature that determine \( F_\lambda \), but \( E_\lambda \) is not one of them. This has the following very important consequence. From (8), we note the
identity \( f_\lambda \equiv \overline{F}_\lambda + T S_{IS}(E_\lambda) \), where \( f_\lambda(E_\lambda, T) \equiv -T \ln z_\lambda \) [compare with \( f^{SW}(E_\lambda, T) \) in (1)]. The explicit dependence of \( f_\lambda(E_\lambda, T) \) [or \( f^{SW}(E_\lambda, T) \)] on \( E_\lambda \) must be trivial and due to \( S_{IS}(E_\lambda) \) because of the independence of \( \overline{F}_\lambda \) [or \( f^{SW}(E_\lambda, T) - T S_{IS}(E_\lambda) \)] on \( E_\lambda \). Accordingly, the summation over \( \lambda \) cannot be replaced by a summation over \( E_\lambda \). This disproves SW1.

We now deal with the summation over \( \lambda \) in (10) in a standard manner. Let \( N(\mathcal{F}) \) denote the number of ISC’s at a given \( T \) with the same \( \mathcal{F} \equiv E_\lambda + \overline{F}_\lambda(T) \). The PF \( Z \) is dominated by the ISC’s of free energy \( \mathcal{F} \) for which \( \mathcal{F} - T S \) is minimum over \( \mathcal{F} \); here \( S(\mathcal{F}) \equiv \ln N(\mathcal{F}) \). The condition for this minimum at \( \mathcal{F} \) is

\[
(\partial S/\partial \mathcal{F})_{\mathcal{F}} = \beta, \quad T \geq T, \tag{11}
\]

as expected. Here, \( T \) is the temperature at which \( \overline{S} \equiv S(\mathcal{F}) = 0 \). Hence, we finally conclude that the final free energy is given by

\[
F \equiv -T \ln Z \equiv \mathcal{F} - T \overline{S}, \quad T \geq T_b, \tag{12}
\]

where the significance of \( T_b \) will become clear in a moment. It should be obvious at this point that the dominant contribution in (10) mixes ISC’s with different \( E_\lambda \) and \( T_{S}^{(\lambda)} \). For \( T < T \), the system is confined to a single ISC corresponding to a particular value \( \lambda = \sigma \). The minimization of \( \mathcal{F} - T S \) is no longer an issue for \( T < T \), as there is only one ISC \( \sigma \) to consider and the minimization of \( \mathcal{F} = \overline{F}_\sigma \) is already ensured by (9).

It is easy to see that the configurational entropy is

\[
S(T) \equiv \overline{S} + \overline{S}_\sigma + S_b. \tag{13}
\]

As the temperature is lowered, regardless of whether we consider CR or SCL, we must first encounter the case \( \overline{S} = 0 \) at \( T \), so that the system is confined to the single ISC \( \sigma \) as discussed above. At a lower temperature \( T_b \equiv T_{S}^{(\sigma)} \leq T, \overline{S}_\sigma = 0 \), and the system is trapped in a single basin \( j = b \). (Compare \( T_b \) with \( T_{SW} \).) The basin \( j = b \) has its lowest allowed temperature \( T = T_b < T_b \), where the basin entropy \( S_b = 0 \). The configurational entropy vanishes when all three components in (13) vanish. This obviously happens at \( T = T_b < T_b \). For CR, \( T_b = 0 \), and for SCL, \( T_b = T_K > 0 \), as proven recently [9]. We now restrict our discussion to SCL and consider \( T_b \leq T < T_b \), so that \( \overline{S}_\sigma = 0 \) and the system is trapped in the basin \( j = b \) whose IS is at \( E_K \) and \( T_b = T_K \). In this basin, \( \mathcal{S} \) remains satisfied until \( T \geq T_K \), but ceases to work below \( T_K \), if we insist that \( E < E_K \) is not allowed. However, if we do allow \( E < E_K \), which requires a mathematical continuation of SCL free energy function below \( T_K \) (which is not equivalent to the continuation of the SCL state itself as it does not exist below \( E_K \)), we can continue to impose \( \mathcal{S} \). This will produce a negative entropy continuation of the SCL-entropy down to absolute zero, which is what all analytical calculations show in which the SCL free energy is obtained by continuing the disordered phase free energy below \( T_M \). However, demanding that \( \mathcal{S} \) continue to operate below \( T_K \), and at the same time demanding that \( E \) remains fixed at \( E = E_K \) is not legal. Similar arguments apply to the consideration of \( \overline{S} \) and \( T_b \). We cannot demand \( \mathcal{S} \) to remain operative below \( T_b \); it must be replaced by \( \mathcal{S} \).
It should be noted that the general landscape picture itself is not capable of providing any information about whether \( T_K > 0 \) or not. For this, we must turn to other approaches like the one developed by Gujrati\[8\] or to some model landscapes. Indeed, model landscapes can be easily constructed in which the temperature associated with the minimum of a basin need not vanish \[13\].

In summary, we have shown that when the landscape picture is carefully developed, there is no conflict with the exact and rigorous results about \( T_K \). In the process, we have also corrected some of the flaws in the SW analysis. As the current analysis deals with the free energies and not the energy minima, IS’s play no useful role except possibly at very low temperatures below \( T_S \).

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[1] The configurational entropy \( S(T) \) is the entropy due to the configurational (positional) degrees of freedom in the system and determines its configurational partition function. The temperature at which \( S(T) \) vanishes is defined as the Kauzmann temperature \( T_K \).

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