Complexity Thermodynamics, Equiprobability Principle, Percolation, and Goldstein’s Conjectures

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(Dated: October 12, 2004)

Abstract

The configurational states as introduced by Goldstein represent the system’s basins and are characterized by their free energies \( \varphi(T, V) \) at a given temperature \( T \) and volume \( V \), as we show here. We find that the energies of some of the special points (termed basin identifiers here) like the basin minima, maxima, lowest energy barriers, etc., which do not appear in the partition function so that the latter is independent of them, cannot be used to characterize the configurational states of the system in all cases due to their possible non-monotonic behavior as we explain. The complexity \( S(\varphi, T, V) \), the natural log of the number of basins having the same free energy \( \varphi(T, V) \), represents the configurational state entropy. We prove that the equilibrium entropy \( S(T, V) \equiv S(\varphi_{0}, T, V) + S_{h}(T, V) \), where \( S_{h} \) and \( \varphi_{0} \) are the equilibrium basin entropy and free energy, respectively. We further prove that all basins at equilibrium have the same equilibrium basin energy \( E(T, V) \) and entropy \( S_{h}(T, V) \). Here, \( \varphi \) and \( E \) are measured with respect to the zero of the potential energy. The equilibrium complexity is shown to be purely an entropic quantity, and not a free energy. The Boltzmann equiprobability principle is shown to apply to the basins in that each equilibrium basin has an equal probability \( P = \exp(-S) \) to be explored. This principle allows us to interpret the basins and their free energy \( \varphi \) as the analogs of the microstates and their energy in the microcanonical ensemble. In addition, it allows us to draw some useful conclusions about the time-dependence in the system. We discuss the percolation due to basin connectivity and its relevance for the dynamic transition. Our analysis validates modified Goldstein’s conjectures that (i) the basin free energy measured with respect to the potential energy of the basin minimum is insensitive to the basin minimum energy, and (ii) the equilibrium basin free energy \( \varphi_{0} \) is insensitive to basins being explored. Thus, our approach demonstrates that the configurational state description is not only formally exact, but also analogous to the conventional approach using microstates. All the above results are shown to be valid at all temperatures, and not just low temperatures as originally proposed by Goldstein.

I. INTRODUCTION

In classical statistical mechanics, the Hamiltonian \( \mathcal{H}(p, q) \equiv K(p) + E(q) \) of a system of \( N \) particles in a fixed volume \( V \) is a sum of the kinetic energy \( K(p) \) and the potential energy \( E(q) \) of the particles; here \( p \) and \( q \) represent the collective momenta and positions of the particles, respectively. The dimensionless total canonical partition function (PF) \( Z_{N}(T, V) \) of the system can be written as a product of two independent integrals

\[
Z_{N}(T, V) \equiv \left( \frac{1}{(2\pi \hbar)^{3N}} \int e^{-\beta K(p)} dp \right) \int e^{-\beta E(q)} dq.
\]

Here \( dp, dq \) represent integrations with respect to the collective momenta and positions of the particles, and \( \beta \) the inverse temperature \( 1/T \) in the units of the Boltzmann constant \( k_{B} \).

A. Kinetic PF

The first integral \( Z_{N,KE}(T) \) (including the prefactor) in the square brackets in (1) contains no interaction energy, and is trivial to evaluate because of the quadratic nature of \( K(p) \). It is clearly independent of the volume \( V \). The corresponding free energy \( F_{N,KE}(T) \equiv -T \ln Z_{N,KE}(T) \) is the free energy due to the kinetic energy and is the same for all systems, regardless of their potential energy of interaction, and volume. The corresponding entropy \( S_{N,KE}(T) \equiv -(\partial F_{N,KE}(T)/\partial T) \) and energy \( E_{N,KE}(T) \equiv F_{N,KE}(T) + TS_{N,KE}(T) \) are independent of \( V \), and have the same values for all systems. Therefore, we do not have to specifically take into account the contribution from the kinetic energy part. All we need to do in this case is to add the contribution \( F_{N,KE}(T) \) to the free energy from the second integral in (1) at the end of the calculation. This is precisely what we do here and mostly consider the configurational PF discussed below.

B. Configurational PF

The dependence on the potential energy (PE) in the PF \( Z_{N}(T, V) \) is through the second integral \( Z_{N}(T, V) \) (the prime indicating integration over distinct configurations of the particles), conventionally called the configurational PF:

\[
Z_{N}(T, V) \equiv \int q e^{-\beta E(q)} dq.
\]

The configurations of the system are represented by phase points in the phase space \( \Gamma_{N}(V) \) defined by the position coordinates \( q \). Each phase point represents a
microstate of the system. By appending another axis to $\Gamma_N(V)$ to represent the potential energy $E(q)$ of each point $q$, we introduce a $3N$-dimensional energy surface $\Sigma_N(V)$ in a $(3N + 1)$-dimensional landscape space $\Lambda_N(V)$. The height of the PE surface represents the potential energy $E$ of each phase point in the space $\Gamma_N(V)$. Thus, each configuration or microstate is characterized by its potential energy $E$, along with $V$ and $N$; the particle number $N$ is kept fixed in this work. For the moment, let us keep $V$ fixed and consider the slice $d\Sigma_N(E, V)$ of the surface $\Sigma_N(V)$, with energies between $E$ and $E + dE$. The slice is given by the intersection of $\Sigma_N(V)$ with the two parallel constant energy surfaces $\Sigma_N(E)$ and $\Sigma_N(E + dE)$ of energy $E$ and $E + dE$, respectively, in $\Lambda_N(V)$. This slice defines the microcanonical ensemble corresponding to energy $E$ and, according to Boltzmann [1], all configurations or microstate are equiprobable to be explored by the system. In the canonical, i.e., the $NTV$-ensemble, the entire surface $\Sigma_N(V)$ uniquely determines the thermodynamics of the system, and is therefore of central importance. This point has been made forcefully in the context of glasses in a recent work [2] to which we direct the reader.

In equilibrium, only configurations that have their energies $E$ equal to the equilibrium energy $E(T, V)$ determine the thermodynamics. These are what we will call the equilibrium configurations at $T$. The equilibration process, therefore, is highly selective and picks out only the equilibrium configurations that change from one temperature to another; we are of course neglecting the thermal fluctuations. It is well known [1] that the energy fluctuations $\Sigma E$ at constant $V, N$ is given by $T\sqrt{C_{V,N}}$, where $C_{V,N}$ is heat capacity at constant $V, N$. Thus, the relative fluctuation $\Sigma E/E(T, V)$ behaves as $1/\sqrt{N}$ for any finite $T$. This justifies our neglecting the fluctuations for a macroscopic system.

In the following, we will only consider a macroscopic system for which $N$, and $V$ are very large. The thermodynamic limit, which will be implicit in the following, requires considering $N \to \infty, V \to \infty$ such that $n \equiv N/V$ is kept fixed in the canonical, i.e., the $NTV$-ensemble. In the related $NTP$-ensemble, we only require $N \to \infty$. We will usually suppress the index $N$ (but continue to show $V$) in the following for simplicity.

C. Goldstein’s Ideas and Basin Identifiers

We follow Goldstein and consider the $NTV$-ensemble. The PE surface $\Sigma(V)$ contains many local minima whose importance has been argued by Goldstein [3, 4] for supercooled liquids. He also provided a qualitative description of the nature of the resulting landscape created by the distribution of minima and drew attention to the idea of configurational states, which are associated with PE minima in $\Sigma(V)$. The potential wells containing the minima are known as basins or valleys. The configurational states are collections of allowed configurations within a basin. Therefore, the equilibrium configurational states must contain only equilibrium configurations of energy $E = E(T, V)$. However, because of the importance of the basin minima (BM) at low temperatures, Goldstein has postulated that the configurational states, instead of being associated with the entire basins, are characterized by the basin minima (BM), and in particular by their energy $E_L$. The BM are not the only point of interest in basins; the latter have other points of interest such as the lowest energy barrier (LB) or the most probable energy barriers (MPB), i.e. the barriers with the highest population, which are bound to play an important role in crossover dynamics or diffusion, as the temperature is raised; this point is discussed further in the last section. Thus, one can also take the energy $E_{LB}$ corresponding LB or $E_{MPB}$ corresponding to MPB to characterize the basin depending on the temperature range. One can also take the highest energy $E^H$ of the basin, the highest barrier (HB) energy $E^{HB}$, or the energy of some other special basin point to characterize the basin. In the following, we will use the term basin identifier to refer to any of the special points of the basins and denote the corresponding energy by $E$.

It is obvious that each basin identifier has its usefulness limited to a certain temperature range. Thus, as the temperature is raised, different identifiers and their energies become relevant and to focus on only just one of the identifiers like BM will have a limited applicability. To provide a description of the system that is useful at all temperatures, we need to focus on the basin free energy which is determined by the shape and topology of the basins. This will require a methodology to express the basin free energy in terms of the equilibrium energies of an identifier in its temperature range. One of our aims here would be to describe such a methodology.

The shape and topology uniquely determine the free energy of the basins at all temperature, which then uniquely determine the thermodynamics of the viscous fluid. Because of this, we will describe the configurational states by specifying the basin free energy so that the characterization remains valid at all temperatures. Later on, we will see that we can also use the basin energy to represent the configurational states, because the equilibrium configurations are identified by the equilibrium energies, as said above.

The main motivation behind the introduction of configurational states appears to be the ability to express the entropy as a sum of two different contributions at low temperatures where the system is confined to one of the basins [3]. This partitioning requires the two contributions to be independent. Could such a partition and the independence of its two parts be valid at all temperatures? In his analysis, Goldstein who only considers BM as the basin identifier to characterize the basin has listed several conjectures that were common in the field [4] at the time and are expected to be valid at low enough temperatures.

(C1) The basin free energy is independent of the possible
basin being explored.

(C2) The basin free energy is particularly independent of the basin's potential energy minimum $E_L$.

(C3) The partition function is a product of the basin and the BM partition functions $z_b(T,V)$, and $Z_{BM}(T,V)$, respectively.

The BM PF $Z_{BM}$ [4] is defined as

$$Z_{BM}(T,V) = \int N_{BM}(E_L,V)e^{-\beta E_L}dE_L.$$  \hspace{1cm} (3)

Here, $N_{BM}(E_L,V)dE_L$ represents the number of potential energy minima in the energy range $E_L$ and $E_L+dE_L$. However, the basin PF $z_b$ is left undefined. From the form of $Z_{BM}$ in (3), it is most certain that $z_b$ for a given basin is defined by considering energies measured with respect to the basin minimum [7]. Goldstein emphasizes that basin anharmonicity or the curvature at its minimum [6] may be very important and should be included in $z_b$. According to (C1), all equilibrium basins have the same basin free energy $f_b(T,V) = -T\ln z_b$. According to (C2), $f_b(T,V)$ is independent of PE minima of the equilibrium basins. This conjecture merely reflects the fact that $f_b(T,V)$ is measured with respect to the basin energy minimum [7]. According to (C3), the PF [without $Z_{KE}(T)$] is given as a product [4, 5]

$$Z(T,V) = z_b(T,V)Z_{BM}(T,V).$$  \hspace{1cm} (4)

The form of $Z_{BM}$ in (3) implies the equiprobability hypothesis that basins having their BM at the same $E_L$ are equiprobable. Can these conjectures be justified at all temperatures?

Our aim in this work is to provide a unified formalism that remains valid at any temperature. As we will see, this will require modifying the above conjectures slightly, which can then be shown to be valid at all temperatures.

1. **Condition of Equilibrium and T-Dependence**

**Remark 1** For a macroscopic system in equilibrium, the PF must be maximized.

We apply this condition to $Z_{BM}(T,V)$. In equilibrium at a given $T, V$, it should be dominated by basins having their minima at the equilibrium minima energy $E_L(T,V)$ at which the integrand in (3) is maximum. In terms of the BM entropy $S_{BM}(E_L,V) \equiv \ln N_{BM}(E_L,V)$, $E_L(T,V)$ is determined by

$$\left[\left(\partial S_{BM}(E_L,V)/\partial E_L\right)_{V,N}\right]_{E_L=E_L(T,V)} = \beta, \hspace{1cm} (5)$$

which is the condition of equilibrium. The equilibrium BM entropy $S_{BM}(T,V)$ in the canonical ensemble is the value of the microcanonical entropy $S_{BM}(E_L,V)$ at $E_L = E_L(T,V)$. Even though $S_{BM}(E_L,V)$ is independent of $T$, the canonical entropy $S_{BM}(T,V) \equiv S_{BM}[E_L(T,V), V]$, obtained after the integrand has been maximized to achieve equilibrium and $E_L$ replaced by its equilibrium value $E_L(T,V)$, is a function of $T$. This is a common feature in statistical mechanics.

**Remark 2** A microcanonical quantity is independent of $T$ but becomes $T$-dependent in the canonical ensemble through its dependence on some equilibrium quantity such as the $T$-dependence of $S_{BM}(E_L,V)$ at $E_L = E_L(T,V)$ above.

2. **Basins at Equilibrium**

Provided (C3) is valid, the basins that contribute at equilibrium have the same equilibrium BM energy $E_L = E_L(T,V)$ and are equally probable. The BM free energy $F_{BM}(T,V) \equiv -T\ln Z_{BM}(T,V)$ is given by

$$F_{BM}(T,V) = E_L(T,V) - TS_{BM}(T,V),$$

and the configurational free energy $F(T,V) = -T\ln Z(T,V)$ is given by the sum

$$F(T,V) = f_b(T,V) + F_{BM}(T,V) = \left[e_b(T,V) + E_L(T,V)\right] - T[S_b(T,V) + S_{BM}(T,V)],$$

where $e_b(T,V)$ and $S_b(T,V)$ are the equilibrium basin energy (measured with respect to the basin minima) and entropy, respectively. The first quantity, therefore, represents the equilibrium basin energy measured with respect to the zero potential. Adding to this $F_{KE}(T) \equiv E_{KE}(T) - TS_{KE}(T)$ from the kinetic PF, we obtain the free energy

$$F(T,V) = -T \ln Z(T,V)$$

$$= E\vib(T,V) - T[S\vib(T,V) + S_{BM}(T,V)],$$

where $E\vib(T,V) = E_{KE}(T) + e\vib(T,V) + E_L(T,V)$, and $S\vib(T,V) = S_{KE}(T) + S_b(T,V)$ represent the equilibrium basin vibrational energy and entropy, respectively.

Within the approximation implied in (C3) which is expected to be valid at low temperatures, we observe that the equilibrium entropy $S(T)$ in the above free energy $F(T,V)$ or $F(T,V)$ is a sum of two parts, one of which is the configurational state entropy $S_{BM}(T,V)$, and the other one is $S\vib(T,V)$ or $S_b(T,V)$, respectively. Thus, the approximation in (C3) and the entropy additivity are equivalent in the above approach.

D. A Different Approach

According to Goldstein, we can interpret the thermodynamics of the system as being confined to any of the many basins; this is certainly expected to be valid at least at low temperatures. His seminal ideas based on
the above conjectures (C1-C3) have been central in understanding glasses or amorphous materials, as they provide an intuitive rational for the observed relaxation of two different time-scales [3, 8]. Using these ideas, Goldstein was able to provide an interesting and sufficiently tractable scheme for calculation discussed above, and made some quantitative predictions [3, 4]. Our interest here is to check the validity of the above conjectures, to see if they are valid at all temperatures, and to shed new light on some of the core concepts, like the basin free energy, the nature and significance of configurational states and their relationship with the basin energy or free energy, the à priori equiprobability of the basins in equilibrium and their energies and entropies, etc. We also discuss the phenomenon of percolation of basin connectivity and its possible connection with the dynamics in the system.

We carry out an analysis by taking an approach which has appeared in the literature [9–12], but has not been studied extensively. In particular, we measure the basin free energy with respect to a common reference energy, the zero of the potential energy (see below) and denote it by \( \phi_b(T, V) \) to distinguish it from the previous free energy \( f_b(T, V) \). The approach leads to the equiprobability theorem in a straightforward manner. This is highly pleasing as it brings forth the similarity with the conventional equiprobability hypothesis due to Boltzmann [1].

We substantiate the first two conjectures of Goldstein in slightly different forms; the third conjecture also needs to be modified. All these are shown to be valid at all temperatures.

1. Complexity

As said above, Goldstein’s ideas seem to justify a well-accepted belief in the glass community that the entropy of the supercooled liquid is a sum of two contributions: (i) the entropy \( S_{BM}(T, V) \) due to different equilibrium configurational states or basins, and (ii) the entropy \( S_b(T, V) \) associated with an equilibrium basin. (The supercooled liquid is a metastable liquid, which is described by the landscape in which some of the basins that are relevant for the crystal phase are deleted from consideration.) However, whether such a partition actually occurs in viscous liquids has never been rigorously demonstrated. (As we will see here, the actual rigorous demonstration is not trivial.) Borrowing ideas from the spin-glass field, Mézard and Parisi [9] introduced the idea of complexity \( \overline{S}(T, V) \) as a candidate for the entropy of equilibrium configurational states, which has been adopted by other workers in the field; see, for example, [11, 12]. The complexity is determined not by the BM energies \( E_b \), (or the energies of other basin identifiers such as \( E_{LB}^{MPB} \), \( E_{MPB}^{LB} \), etc.) but by the basin free energies; see below. Coluzzi et al [10] gave a plausibility argument that the liquid’s equilibrium entropy \( S(T, V) \) is a sum of the complexity \( \overline{S}(T, V) \) and \( S_b(T, V) \):

\[
S(T, V) = \overline{S}(T, V) + S_b(T, V) .
\]

Coluzzi and coworkers [11] have given a numerical scheme to evaluate complexity directly by making several hypotheses, one of which is the equiprobability of the basins of the same free energy, and another one is the above entropy partition (7).

2. Present Goal

Since it appears, from all accounts, that the central idea of configurational states or basins and the complexity are important concepts that play a pivotal role in the thermodynamics at low temperatures and hopefully help us unravel the mystery of glassy states, it is also important to demonstrate that the above partition in (7) is valid rigorously and that the equiprobability hypothesis can be justified on general grounds not only at low temperatures but at all temperatures. The latter allows us to treat the basin free energy \( \phi(T, V) \) in the same manner as the energy in the microcanonical ensemble because of the equiprobability of configurations of the same energy in that ensemble. The partitioning of \( S(T, V) \) replaces the third conjecture of Goldstein.

We will prove the following statements.

(S1) The basin free energy \( f_j(T, V) \) of the \( j \)-th basin is independent of the energy of a particular basin identifier, like the BM energy.

(S2) The equilibrium basin free energy \( \phi_b(T, V) \), energy \( E_b(T, V) \), and entropy \( S_b(T, V) \) are the same in all equilibrium basins that are explored at a given \( T, V \).

(S3) All equilibrium basins have equal probability of being sampled.

(S4) The entropy partition (7) is a general result.

We discuss the general topological features of the landscape in the next section, and write down the fundamental thermodynamic differential relations. We then compare this analysis with the standard analysis, which is carried out in Sect. III. The results are discussed in the last section, which also contains some speculative comments and a short summary of our results.

II. GOLDSTEIN’S LANDSCAPE

A. Analysis

The surface \( \Sigma(V) \) can be formally decomposed into nonoverlapping basins \( B_j(V) \). There would be an energy barrier between different neighboring minima. In each basin \( B_j(V) \), the allowed energy range is \( \Delta_j E = \ldots \)
\( E^H - E_{LJ} \), where \( E^H_j \) and \( E_{LJ}(V) \) are the highest and lowest allowed energies in \( B_j(V) \) [13]. The highest energy also represents the highest barrier energy in the basin. The exceptions are the basins that contain particles near the walls of the container (of volume \( V \)) in which the interactions of the particles with the walls will make the potential very large (\( \to \infty \)) in order to confine the particles. For such basins, \( E^H_j \to \infty \). In this case, the highest energy does not represent the highest barrier to some other basin. The lowest energy in a basin does not necessarily have to be point-like in that it is associated with only one phase space point \( \mathbf{q} \). It is possible that there are many contiguous phase space points, all having the same lowest energy, with no energy barrier between them such as the minima in an inverted Mexican hat. In this case, all these points would be classified as representing a single minimum and belonging to a single basin. The same situation may also occur for other points like the points of highest energy, the energy barriers, etc. The number of basins in \( \Gamma(V) \) will be denoted by \( N_B(V) \). The canonical partition function \( Z(T, V) \) can be formally expressed in the form of an identity as a sum over the basins:

\[
Z(T, V) = \sum_{j=1, N_B(V)} Z_j(T, V), \tag{8}
\]

where

\[
Z_j(T, V) = \int_{B_j(V)} d\mathbf{q} e^{\beta E(\mathbf{q})} \tag{9}
\]

is the PF of the \( j \)-th basin \( B_j(V) \), and the integration is over the coordinates confined within the basin. The energy is measured with respect to a common zero of potential for all basins, and not with respect to some predetermined \( E_j(V) \) associated with a basin identifier. We denote the basin free energy by \( \phi_j(T, V) = -T \ln Z_j(T, V) \) and introduce \( f_j(T, V) = \phi_j(T, V) - E_j(V) \), which represents the basin free energy measured from \( E_j(V) \). The probability \( P_j(T, V) \) that the system under equilibrium explores the basin \( B_j(V) \) is given by

\[
P_j(T, V) = Z_j(T, V)/Z(T, V). \tag{10}
\]

**B. Fundamental Thermodynamic Relations**

1. **Basins**

Let us rewrite (9) in a different way as follows. Consider the surface \( \Sigma_j(V) \), which is the part of the surface \( \Sigma(V) \) that belongs to the basin \( B_j(V) \). The surface \( \Sigma_j(V) \) exists for energies in the range \( \Delta_jE \). We project it on the 3N-dimensional phase space \( \Gamma(V) \), which is orthogonal to the \( E \)-axis. The projection \( \Pi_j(V) \) determines the number of configurations (not to be confused with the configurational states of Goldstein) of the system that belong to the basin as follows. Consider the slice \( d\Sigma_j(E, V) \) of the surface \( \Sigma_j(V) \) between the energies \( E \) and \( E + dE \). The slice contains all the points in \( \Sigma_j(V) \) that lie between the intersections (known as the turning points in classical mechanics) of \( \Sigma_j(V) \) with the two parallel constant energy surfaces \( \Sigma(E) \) and \( \Sigma(E + dE) \) that were introduced above, and will be closed (in the sense that a ring is) if the slice cuts the basin in all directions; otherwise it is open. For energies close to \( E_{LJ}(V) \), the slice is closed, but becomes open as we get to higher energies and eventually disappears at \( E^H_j(V) \). The projection \( d\Pi_j(E, V) \) of this slice on \( \Gamma(V) \) is closed (open) if \( d\Sigma_j(E, V) \) is closed (open). The area \( |d\Pi_j(E, V)| \) of the projection determines the number of configurations \( W_j(E, V) dE = |d\Pi_j(E, V)| \) between the energies \( E \) and \( E + dE \). Let us introduce the microcanonical basin entropy function \( S_j(E, V) \equiv \ln W_j(E, V) \), which is independent of \( T \). The entropy \( S_j(E, V) \) at fixed \( V, N \) satisfies the differential relation

\[
dS_j(E, V) = (\partial S_j(E, V)/\partial E)_{V, N} dE. \tag{11}
\]

Now, we can rewrite (9) as follows:

\[
Z_j(T, V) = \int_{E \in \Delta_jE} dE \exp[S_j(E, V) - \beta E(V)].
\]

For a macroscopic system at fixed \( T \), the integral is dominated by the maximum integrand at \( E = E_j(T, V) \) (see Remark 1), given by

\[
\left[(\partial S_j(E, V)/\partial E)_{V, N}\right]_{E=E_j(T,V)} = \beta, \tag{12}
\]

which is the standard thermodynamic relation between the entropy and temperature; compare with (5). The energy \( E_j(T, V) \) represents the average basin energy at a given temperature \( T, V \); and \( N \). (We will reserve the usage of the term ”equilibrium” for a thermodynamic quantity only after the PF \( Z(T, V) \) has been evaluated. To make this distinction, we use the term ”average” at this stage.) Let us introduce the energy difference \( \Delta E_j = E - E_j \), and \( \Delta E_j(T, V) = E_j(T, V) - E_j \), for the \( j \)-th basin, where \( E_j \) is the energy of some particular basin identifier like BM, LB, etc. We can rewrite (12) as

\[
\left[(\partial S_j(E, V)/\partial E)_{V, N}\right]_{\Delta E_j=\Delta E_j(T,V)} = \beta. \tag{13}
\]

The canonical basin entropy \( S_j(T, V) \) is given by the microcanonical basin entropy evaluated at the average energy \( E = E_j(T, V) \):

\[
S_j(T, V) = S_j[E_j(T, V), V].
\]

Using (11) at \( E = E_j(T, V) \), and (12), we find that

\[
dE_j(T, V) = T dS_j(T, V) \tag{14}
\]

at fixed \( V, N \). The average basin free energies \( \varphi_j(T, V) \) and \( f_j(T, V) \equiv \varphi_j(T, V) - E_j \) are given by

\[
\varphi_j(T, V) = E_j(T, V) - T S_j(T, V), \tag{15a}
\]

\[
f_j(T, V) = \Delta E_j(T, V) - T S_j(T, V), \tag{15b}
\]
A given $T$ corresponds to a particular value of $\Delta E_j(T, V)$ [see (13)] measured from $\mathcal{E}_j$. Thus, $\Delta E_j(T, V)$ will remain the same even if the value of $\mathcal{E}_j$ is changed by shifting the origin of the energy. In other words, $\Delta E_j(T, V)$ and the average basin free energy $f_j(T, V)$ do not depend on $\mathcal{E}_j$. This proves our statement (S1). Consequently, $\varphi_j(T, V) \equiv f_j(T, V) + \mathcal{E}_j$ depends linearly on $\mathcal{E}_j$. Using (11), (12), and (14), it is easy to obtain the following fundamental differential relation at constant $V, \phi, N$:

$$d\varphi_j(T, V) = df_j(T, V) = -S_j(T, V) dT.$$  

(16)

This gives the change in the basin free energy due to the temperature change within the basin $B_j(V)$.

2. Complexity Analysis

At a given $T, V$ (and $N$), the basin free energy $\varphi_j(T, V)$ varies from basin to basin; hence, $\varphi_j(T, V)$ represents a family of functions, one for each $j$. Let $\varphi \equiv \varphi(T, V)$ represent one of the various functions $\varphi_j$s in this family, and $N(\varphi, T, V)$ the number of basins having the same free energy $\varphi$ for a given $T, V$, regardless of whether $\mathcal{E}_j$ is the same or not for these basins. In other words, these basins need not all have the same basin identifier energy $\mathcal{E}_j = \mathcal{E}$. We now rewrite (8) as

$$Z(T, V) \equiv \sum_\varphi N(\varphi, T, V) e^{-\beta \varphi}.$$  

(17)

For a macroscopic system, we expect the family of functions represented by $\varphi(T, V)$ to be almost continuous "over" the basin index $j$. This is an assumption that is expected to remain valid even at low enough temperatures. With this assumption, the sum in (17) can be replaced by an integration over this family.

Let us introduce the complexity $S(\varphi, T, V) \equiv \ln N(\varphi, T, V)$, which satisfies the following differential relation at constant $V$ and $N$:

$$dS(\varphi, T, V) = \langle \partial S/\partial \varphi \rangle_{T, V} d\varphi + \langle \partial S/\partial T \rangle_{\varphi, V} dT.$$  

(18)

For a macroscopic system at fixed $T, V$, see Remark 1, the PF in (17) is dominated by that particular value of the basin free energy, which we denote by $\varphi_b \equiv \varphi_b(T, V)$, for which the summand (or integrand) is maximum, i.e. $\Phi(\varphi, T, V) \equiv \varphi - TS$ is minimum. The basins having this free energy $\varphi_b(T, V)$ represent the equilibrium basins determining the thermodynamics at fixed $T, V$. As said above, these equilibrium basins are not required to have the same basin identifier energy $\mathcal{E}_j = \mathcal{E}$. The location of the maximum at $\varphi = \varphi_b$, for continuous $\varphi$, is determined by

$$\left[\langle \partial S(\varphi, T, V)/\partial \varphi \rangle_{T, V}\right]_{\varphi = \varphi_b(T, V)} = \beta,$$  

(19)

where the derivative is obtained by a variation over the family of function $\varphi$. The temperature $T$ is kept fixed under this variation and is shown explicitly in (19); this was not necessary in (12) since $S_j(E, V)$ did not have an $T$-dependence, even though the variation there was also carried out at fixed $T$. The equilibrium complexity $\overline{\mathcal{S}}(T, V)$ is given by $S(\varphi, T, V)$ evaluated at $\varphi = \varphi_b(T, V)$:

$$\overline{\mathcal{S}}(T, V) \equiv S[\varphi_b(T, V), T, V].$$  

(20)

(Here, we have used an overbar to indicate that $\overline{\mathcal{S}}(T, V)$ is a function of two variables, while $S[\varphi_b(T, V), T, V]$ is a function of three variables.) Each equilibrium basin has the same free energy $\varphi_b$. This proves a part of our statement (S2).

3. Basin Entropy and Complexity

We can invert the function $S(\varphi, T, V)$ over the entire positive temperature range where it is monotonically increasing with $\varphi$, see (19), and express $\varphi$ as a function of $S : \varphi \equiv \varphi(S, T, V)$ over this range. Accordingly, the change in $\varphi$ due to changes in the complexity $\mathcal{S}$ and $T$ is given by

$$d\varphi(S, T, V) = \langle \partial \varphi / \partial S \rangle_{T, V} dS + \langle \partial \varphi / \partial T \rangle_{S, V} dT.$$  

(21)

In equilibrium, $\varphi$ and $\mathcal{S}$ should be replaced by $\varphi_b$ and $\overline{\mathcal{S}}$ respectively, and the coefficient of $d\overline{\mathcal{S}}$, according to (19), should be $T$. From (18), we note that at equilibrium

$$\langle \partial \varphi_b / \partial T \rangle_{\overline{\mathcal{S}}, V} = -T \langle \overline{\mathcal{S}}(T, V) / \partial T \rangle_{\varphi_b, V}.$$  

In the identity

$$\left( \frac{\partial \varphi_b}{\partial T} \right)_\overline{\mathcal{S}, V} = \left( \frac{\partial \varphi_b}{\partial T} \right)_T + \left( \frac{\partial \varphi_b}{\partial T} \right)_S \left( \frac{\partial \overline{\mathcal{S}}}{\partial T} \right)_V,$$  

obtained from (21), the first term on the right represents the change in the equilibrium basin free energy, see (16), solely due to the temperature change $dT$ within a basin; the contribution from the complexity change due to $dT$ is given by the second term. Thus, the first term is the negative of the basin entropy $S_b(T, V)$, and we have

$$T \left( \frac{\partial \overline{\mathcal{S}}}{\partial T} \right)_{\varphi_b, V} = S_b(T, V),$$  

(22a)

$$\left( \frac{\partial \varphi_b}{\partial T} \right)_V = T \left( \frac{\partial \overline{\mathcal{S}}}{\partial T} \right)_V - S_b(T, V).$$  

(22b)

4. Free Energy and Entropy

The equilibrium free energy $F(T, V) \equiv -T \ln Z(T, V)$ is given by the value of $\Phi(\varphi, T, V) \equiv \varphi - TS$ at equilibrium, i.e.,

$$F(T, V) \equiv \Phi(\varphi_b, T, V) = \varphi_b(T, V) - T \overline{\mathcal{S}}(T, V).$$  

(23)

Taking its differential at constant $V, (and N)$, we obtain

$$dF(T, V) = d\varphi_b(T, V) - T d\overline{\mathcal{S}}(T, V) - \overline{\mathcal{S}}(T, V) dT$$

$$= -[\mathcal{S}(T, V) + S_b(T, V)]dT,$$  

(24)
where we have used (21) applied to $\varphi_b$. The entropy can be calculated directly from $S(T, V) = -(\partial F/\partial T)_{V}$. From (24), we have

$$S(T, V) = \mathcal{S}(T, V) + S_b(T, V) = \left( \frac{\partial T \mathcal{S}}{\partial T} \right)_{\varphi_b, V},$$

where we have used (22a). Thus, the entropy of the system is a sum of two contributions, which proves our statement (S4). The derivative on the right-hand side in the above equation can also be written as $-(\partial F/\partial T)_{\varphi_b, V}$, which should be identical to the derivative $-(\partial F/\partial T)_{V}$ from the definition of $S$. Thus,

$$(\partial F/\partial T)_{V} \equiv (\partial F/\partial T)_{\varphi_b, V},$$

which shows that the equilibrium free energy $F(T, V)$ is independent of the basin free energy $\varphi_b$ (at fixed $T$). This should come as no surprise since the equilibrium $\varphi_b$ is determined by the condition

$$(\partial F/\partial \varphi_b)_{T, V} \equiv (\partial F/\partial \varphi)_{T, V} = 0. \quad (25)$$

We can now include the kinetic energy part of the free energy to obtain the complete free energy

$$F(T, V) \equiv -T \ln Z(T, V) = \{E_b(T, V) + E_{KE}(T)\}
-T[S_b(T, V) + S_{KE}(T)] - T\mathcal{S}(T, V).$$

The quantity in the curly brackets represents what is conventionally called the equilibrium vibrational free energy, even though one can be sure of its vibrational nature only at low temperatures where we expect the projections $d\Pi_j(E, V)$ of each contributing basin to be closed (for vibrations, the basin must confine the motion in all directions, which may not be possible at high temperatures). The last term is the contribution due to the complexity.

5. **Equilibrium Identifier Energy $\mathcal{E}(T, V)$**

The equilibrium basin identifier energy $\mathcal{E}(T, V)$ is, by definition, given by

$$\mathcal{E}(T, V) \equiv \sum_{j=1,N_b(V)} \mathcal{E}_j(V)\mathcal{P}_j(T, V). \quad (26)$$

It is clear that this equilibrium value cannot be expressed as a derivative of the partition function. It is easily remedied. We add a dimensionless parameter $\lambda$ that couples to the basin identifier energy $\mathcal{E}_j$ so that there is an additional term $\lambda \mathcal{E}_j$ in the energy, and define a modified PF

$$Z(\lambda, T, V) \equiv \sum_{j=1,N_b(V)} e^{-\lambda \mathcal{E}_j(V)} Z_j(T, V). \quad (27)$$

The equilibrium $\mathcal{E}(T, V)$ is given by

$$\mathcal{E}(T, V) \equiv -T[\langle \partial \ln Z(\lambda, T, V) / \partial \lambda \rangle_{T, V}]_{\lambda=0}. \quad (28)$$

In the limit $\lambda \to 0$, this modified PF reduces to the earlier PF in (8). For $\lambda > 0$, basins with lower identifier energies are weighted more than the higher ones, with the reverse true for $\lambda < 0$. For $\lambda = 0$, there is no preference for any particular value of $\mathcal{E}_j$; recall that $Z_j(T, V)$ does not depend on $\mathcal{E}_j$. It is obvious that the sum in (26) can be limited to only equilibrium basins for a macroscopic system. For equilibrium basins, all allowed values of $\mathcal{E}_j$ are equally probable and will result in the maximum spread $\Delta \mathcal{E}$ in the possible values of $\mathcal{E}_j$ under the summation in (26).

Thus, it appears that the spread in the allowed values of $\mathcal{E}_j$ may very well be of the order of $N$, and not $\sqrt{N}$. In other words, the summand in (26) is most probably not peaked sharply at some particular value of $\mathcal{E}_j$; see also Sect. IV(D) below. We hope to answer this question in future.

It is easy to show from (26) that

$$T^2 \frac{\partial \mathcal{E}(T, V)}{\partial T} = \sum_{j=1}^{N_b(V)} \Delta \mathcal{E}_j(V) \Delta \mathcal{E}_j(T, V) \mathcal{P}_j(T, V), \quad (28)$$

where $\Delta \mathcal{E}(T, V) \equiv \mathcal{E}(T, V) - \mathcal{E}(T), \Delta \mathcal{E}_j(T, V) \equiv \mathcal{E}_j(T, V) - \mathcal{E}(T, V)$, and $\mathcal{E}(T, V)$ is the equilibrium energy of the system. Thus, the derivative is a cross-correlation between two fluctuations, $\Delta \mathcal{E}_j(T, V)$ and $\Delta \mathcal{E}_j(T, V)$. Since cross-correlations do not usually have a fixed sign, there is no theoretical reason for $\mathcal{E}(T, V)$ to be a monotonic increasing function of $T$. This does not mean that the above derivative cannot be positive for many physical systems.

We now show the expected result that the equilibrium free energy $F(T, V)$ cannot depend on the identifier energy explicitly by demonstrating that

$$(\partial F/\partial \mathcal{E})_{T, V} = 0; \quad (29)$$

compare with (25). For this, we use $\Phi(\varphi, T, V) \equiv \varphi - T\mathcal{S}$ and obtain

$$(\partial \Phi/\partial \mathcal{E})_{T, V} = (\partial \varphi/\partial \mathcal{E})_{T, V} - T(\partial \mathcal{S} / \partial \mathcal{E})_{T, V},$$

which, from (21), reduces to

$$(\partial \Phi/\partial \mathcal{E})_{T, V} = (\partial \varphi/\partial \mathcal{S})_{T, V}(\partial \mathcal{S} / \partial \mathcal{E})_{T, V} - T(\partial \mathcal{S} / \partial \mathcal{E})_{T, V}.$$
will not be unique, unless some particular scheme is used. We present a way to accomplish this under the condition that $E(T, V)$ is a monotonic function of $T$ in its temperature range. We will, therefore, consider this case below.

The monotonic function $E(T, V)$ of $T$ can be inverted to yield

$$T = T[E(T, V), V].$$

This will allow us to express any function of $T$ as a function of $E(T, V)$. For example, we can express $f_j(T, V)$ as a function $f_j[E(T, V), V]$ of $E(T, V)$. We can similarly express $\varphi(T, V)$ as a function $\varphi_j[E(T, V), V]$ of $E(T, V)$. We can also express $\varphi_b(T, V)$, and $\mathbf{S}(T, V)$ as a function $\varphi_b[E(T, V), V]$, and $\mathbf{S}[E(T, V), V]$, respectively, of $E(T, V)$.

Let $N_{BH}(E, V)dE$ represents the entropy $S_{BH}(E, V)$ which will most probably not represent the entropy $S_{BM}(E, V)$ introduced above in (3). The $T$-dependent basin identifier entropy evaluated at $E = E(T, V)$

$$S_{BH}(T, V) = S_{BH}[E(T, V), V]$$

does not necessarily represent the entropy due to equilibrium basins for which $E = E(T, V)$. The equilibrium basins satisfy the conditions in (S2), but the basins enumerated by $N_{BH}(T, V)$ have no such conditions imposed on them. Moreover, the equilibrium basins have a wide range of allowed basin identifier energies $E_j$ because of $\lambda = 0$, as discussed above. Thus, the entropy due to equilibrium basins with $E = E(T, V)$ is most probably very different from the complexity $\mathbf{S}[E(T, V), V]$ obtained by the above prescription from $S(T, V)$. It is clear that while the basins counted by $N_{BH}(T, V) = N_{BH}[E(T, V), V]$ contain all the equilibrium basins with $E = E(T, V)$, they also contain many other basins not satisfying (S2). Let $N_{BH, NE}(T, V)$ represent the latter non-equilibrium basins. Since not all equilibrium basins in $\mathbf{N}(T, V)$ have $E = E(T, V)$, the number of equilibrium basins $N_{BH, LE}(T, V)$ in $N_{BH}(T, V)$ is such that $N_{BH, LE}(T, V) < N_{BH}(T, V)$. By definition, we have

$$N_{BH}(T, V) = N_{BH, LE}(T, V) + N_{BH, NE}(T, V).$$

The current analysis cannot answer whether the second contribution is thermodynamically insignificant compared to the first contribution in (31); see the discussion of (40) below. To have $N_{BH}(T, V) = N_{BH}(T, V)$ at all temperatures would be a precarious coincidence and hard to justify. Therefore, the sum

$$S_{BH}(T, V) + S_b(T, V)$$

will most probably not represent the equilibrium entropy $S(T, V)$ at all temperatures. For $E = E_L$, $S_{BH}(T, V)$ represents the entropy $S_{BM}(T, V)$ introduced above in (3).

Thus, most probably

$$S(T, V) \neq S_{BM}(T, V) + S_b(T, V)$$

at all temperatures. In other words, $S_{BH}(T, V)$ is most probably not equal to $\mathbf{S}(T, V)$.

As said above, the representation a thermodynamic quantity in terms of $E(T, V)$ is not necessarily unique. Consider, for example, $\mathbf{S}(T, V)$. There is an alternative way to express it in terms of $E(T, V)$ by recalling its fundamental definition $\mathbf{S}(T, V) \equiv S[\varphi_b(T, V), T, V]$ given in (20). We express $\varphi_b(T, V)$ in the form $\varphi_b(E, V)$ to obtain an alternative expression $S_{\varphi_b}(E, T, V) \equiv S[\varphi_b(E, V), T, V]$ for the complexity family in which $E(T, V)$ has been represented simply by $E$. Let us now consider the following derivative

$$(\partial \mathbf{S}/\partial E)_{T,V} = (\partial S_{\varphi_b}(E, T, V)/\partial E)_{T,V} = \beta(\partial \varphi_b/\partial E)_{T,V},$$

which can be obtained from (18), and where we have also used (19). We should recall that $E = E(T, V)$ above.

7. Equiprobability Principle

From (10), and (23), we note that

$$\mathcal{P}_j(T, V) = \exp[-\mathcal{S}(T, V)],$$

for equilibrium basins, so that the system has equal probability $\exp[-\mathcal{S}(T, V)]$ to belong to any of the equilibrium basins in $\mathcal{N}(\varphi, T, V)$. This proves (S3). The basins counted in $\mathcal{N}(\varphi_b, T, V)$ may have different $f_j(T, V) = \varphi_b(T, V) - E_j$, as there is no guarantee that all these basins will have their basin identifier at the same energy. The probability $\mathcal{P}_j(T, V)$ is determined only by $\varphi_b(T, V)$, the free energy of each of the equilibrium basins in (23), which in turn determines $F(T, V)$ and $\mathbf{S}(T, V)$. Comparing with the standard Boltzmann equiprobability principle, we can understand (34) by the following analogy (see also [11]): the equilibrium basins and their free energies play the role of microstates and their energies in the microcanonical ensemble; the basins and their free energies play the role of microstates and their energies in the canonical ensemble.

III. STANDAR Picture

We can rewrite the configurational PF in (2) slightly differently in a form, which is more standard and does not involve individual basins:

$$Z(T, V) = \int dE W(E, V) e^{-\beta E(V)},$$

where $W(E, V)dE$ represents the number of microstates or configurations represented by the the slice $dE$ with energy between $E$ and $E + dE$. We obtain the number of microstates in the slice $dE$ by considering the area of its projection $d\Pi(E, V)$ on $\Gamma(V)$: $W(E, V)dE = |d\Pi(E, V)|$. It is evident that

$$d\Pi(E, V) = \overline{\Delta} \Pi_j(E, V),$$
where the union is over only those basins that do not yield null projections; these are the basins for which \( E \notin \Delta_j E \). The tilde over the union denotes this restriction. Consequently, we have

\[
W(E, V) = \sum_{j=1}^{N_B(V)} W_j(E, V),
\]

(37)

where the tilde has the same meaning as in (36). Introducing the microcanonical entropy \( S(E, V) \equiv \ln W(E, V) \), we conclude (see Remark 1) that the PF in (35) is dominated by the equilibrium energy \( E(T, V) \) for which the integrand is maximum, and gives the equilibrium state. The equilibrium energy is the solution of

\[
[\partial S(E, V)/\partial E]_{E=E(T, V)} = \beta,
\]

(38)

which is obtained by the variation of the integrand at constant \( T, V \). At a given temperature \( T \), only those microstates with energy in the range \( E(T, V) \), and \( E(T, V) + dE \) determine the thermodynamics through the entropy \( S(T, V) \equiv S[E(T, V), V] \). The canonical entropy \( S(T, V) \) along with \( E(T, V) \) determine the equilibrium free energy \( F(T, V) = E(T, V) - TS(T, V) \).

As the kinetic energy is not a part of the energy \( E \), there is an upper bound to the energy [13]. Therefore, the microcanonical entropy \( S(E, V) \) near this upper bound will be a decreasing function of \( E \). This region corresponds negative temperatures according to (38). Since \( S(E, V) \) is an increasing function near the lower end of the energy \( E \), there is expected to be a maximum in \( S(E, V) \) as a function of \( E \). The rising branch of \( S(E, V) \) corresponds to positive temperatures and it is this branch that is of interest in this work.

A. Connection with Landscape: Selectivity

Using (15a) for the basin free energy \( \varphi_b(T, V) \) in (23), and comparing with the above definition of the free energy in the standard picture, we find that

\[
E(T, V) = E_b(T, V).
\]

(39)

The significance of this result is the following. All configurations contributing to the canonical entropy \( S(T, V) \) in the thermodynamic limit have the same equilibrium energy equal to \( E(T, V) \). The above equation (39) shows that these configurations, which can also be classified as belonging to the different basins, as shown in (37), not only have the same equilibrium basin energy \( E_b(T, V) \), but also have the same basin free energy \( \varphi_b(T, V) \); see (20). From (15a), this also implies that they all have the same basin entropy \( S_b(T, V) \). Thus, the landscape thermodynamics is highly selective. At a given \( T \), only those basins contribute to the thermodynamics that have the same \( E_b(T, V), S_b(T, V) \), and \( \varphi_b(T, V) \). This proves our statement (S2) in totality.

B. Equilibrium Basins

Let \( N_B(T, V) \) denote the number of basins for which \( E = E_b(T, V) \in \Delta_j E \). We say that these basins exist at \( T \). Not all these basins will satisfy all the conditions in (S2). The equilibrium basins are the only basins that determine the thermodynamics and must satisfy (S2). The number of these basins is \( \overline{N}(T, V) \equiv N(\varphi_b, T, V) \). Thus, we expect \( \overline{N}(T, V) < N_B(T, V) \). The number of non-equilibrium basins \( N_{NE}(T, V) \) that do not contribute to the thermodynamics of the system but exist otherwise in the above sense is given by their difference:

\[
N_B(T, V) = \overline{N}(T, V) + N_{NE}(T, V).
\]

(40)

Based on general arguments, there is no way to answer whether the second contribution is thermodynamically insignificant compared to the first contribution in (40). All we can be sure of is the following. Because of (7), we know for sure that the equilibrium number of configurations \( W(T, V) = W[E(T, V), V] = \exp[S(T, V)] \) is exhaustively coming from configurations in all the \( \overline{N}(T, V) \) equilibrium basins:

\[
\overline{W}(T, V) = \overline{N}(T, V) \exp[S_b(T, V)].
\]

The number of configurations coming from the \( N_{NE}(T, V) \) non-equilibrium basins is thermodynamically insignificant. This result has no bearing on the relative magnitude of the two terms in (40). It is possible to have \( N_{NE}(T, V) \) significantly larger than \( \overline{N}(T, V) \) in (40) and still have the contribution from the non-equilibrium basins to \( \overline{W}(T, V) \) insignificant compared to \( \overline{W}(T, V) \).

IV. DISCUSSION AND CONCLUSIONS

A. Basin Connectivity and Percolation

We have already noted, see (36), that the projection \( d\Pi(E, V) \) is the union of different non-null components \( d\Pi_j(E, V) \). A component may have more than one disjunctive joins, such as the one from a basin in the form of an inverted Mexican hat discussed earlier. Corresponding to some energy \( E \) is the equilibrium temperature \( T \) such that

\[
E(T, V) = E.
\]

(41)

Because the heat capacity \( C_V \) is non-negative, \( E(T, V) \) is a monotonic increasing function of \( T \) over the positive temperature range, which is what we are interested in here. Thus, increasing(decreasing) \( E \) is the same as increasing(decreasing) \( T \).

The number of components at \( E \) in the union in (36) is \( N_B(E, V) \) introduced earlier. The shape and size of the components and their number change with \( E \). The components \( d\Pi_j(E, V) \) cannot be open; they are either connected together to form a cluster, or are isolated, and
must be closed (in the form of a ring). Two components are connected, when there is no energy barrier separating them [15]. As we reduce $E$ or $T$, these components become disconnected due to the presence of an energy barrier separating them. As Goldstein has pointed out [3], these energy barriers become very important at lower temperatures as we will discuss further in the following. If a component is isolated, this will mean that there is an energy barrier separating this basin from all other basins. At very high energies ($E > E_{CP}$; see [13]) that are higher than all energy barriers, all projections are open, but connected together. It contains only a small number of basins containing particles near the walls. These energies are not of any interest here. As the energy is reduced, some energy barriers are cut by the surfaces $\Sigma(E)$ and $\Sigma(E + dE)$, which produce isolated closed components and will increase the number of components. In the same process, some of the components disappear as their basin minima energy $E_i$ become higher than $E$. This will reduce the number of components. Thus, we expect the number of components to change with $E$.

For a macroscopic system, the above idea of basin connectivity in the $3N$-dimensional phase space must be phrased in a way that makes statistical sense. A basin $i$ is connected to a basin $j$, if the measure of their common opening (along which there is absence of any barrier) is a non-zero fraction of the projection measure $|d\Pi_i(E,V)|$. We will call such openings relevant. The non-zero fraction of the projection measure will add a non-zero entropic contribution to the barrier height. (It is almost impossible for the system to find a barrier along one of the directions out of macroscopically large $3N$ directions over any finite, no matter how long, time; the entropic contribution for such a barrier is zero.) Thus, it is the free energy, and not the energy that becomes relevant for barrier hopping. A relevant opening will have a non-zero probability $P_{ij}$ of a jump $B_i \rightarrow B_j$ from the $i$-th basin to the $j$-th basin. Openings that are zero fraction of the projection will be called irrelevant as $P_{ij} = 0$. It is in the sense of a relevant opening that the two basins will be considered connected below. Connected basins allow the system to probe them without encountering any energy barriers. In the following, we will make distinctions between two kinds of barriers [15]. Barriers whose heights above $E(T)$ are of the order of $T$ can be overcome due to thermal fluctuations ($\Delta E = T\sqrt{C_V}$) and the time required for the jump $B_i \rightarrow B_j$ is less than or equal to the microscopic relaxation time. If the interest is to study dynamics at a much longer range of time, we can treat these barriers as not different from an opening. The barriers whose heights are much higher than $T$ will give rise to activation processes requiring much longer times to jump over the barriers. These high barriers are the ones we consider in the following. The most probable barriers are those barriers that have the maximum probability to be overcome at a given $T$. The barriers whose heights above $E(T)$ are of the order of $T$ will be treated as openings; thus, they are suppressed [15].

It is obvious that the physics of a continuum model requires the system in the diffusive regime to probe various configurations that continuously transform into each other, as long as we are far away from any phase transition or we are in a metastable state obtained by avoiding a transition like the crystallization. Therefore, we expect various basins to be continuously connected to each other in the sense that there is at least one continuous passage from one basin to another through intermediate basins, without any energy barriers to overcome, so that the phase point can move continuously from one basin to the other. This will certainly be the case at high enough energies (that correspond to high enough temperatures). If it were not the case, the system will have to overcome energy barriers using activation processes because of which, it will "jump" from the equilibrium configuration in one basin into another equilibrium configuration of the other basin (with energy barriers between them); the configuration of the new basin is different from that in the old basin in that the new configuration is not in the immediate vicinity of the old one. The high-temperature situation will correspond to all the components in the projection $d\Pi_i(E,V)$ being connected together as one connected cluster. We can visualize this situation as the percolation of the basin slice projections $d\Pi_i(E,V)$ in one macroscopic cluster, called the percolating cluster $D(E,V)$ that spans the entire space $\Gamma(V)$. Here, the percolation occurs between components $d\Pi_i(E,V)$, all of different shapes and sizes.

The entropy of the system $S(E,V)$ is determined by the percolating cluster $D(E,V)$ at high enough energies. There are other finite clusters or isolated components in addition to $D(E,V)$. But not all components and clusters are thermodynamically significant and contribute to the entropy. Only those components contribute that have the same $E(T,V)$, $S_b(T,V)$, and $\varphi_b(T,V)$. Because of the continuity in the diffusive regime, we expect these components to be part of $D(E,V)$. The number of such components is given by $N(\varphi_b, T, V)$. At high energies, $\varphi(T,V)$ contains disordered configurations pertinent for the liquid state. The percolating cluster allows the system to probe all of the connected equilibrium basins that occur in the diffusive regime.

As we reduce the energy, some of the connected components (i) disappear since they no longer exist ($E < E_L$), (ii) appear since their energy range contains the energy $E$ ($E_L < E < E^H$), or (iii) begin to get disconnected from others due to the emergence of high energy barriers, but the percolating cluster $D(E,V)$ persists in $d\Pi(E,V)$ although it is of a different size. It may happen that some basin components get completely isolated from each other and the percolating cluster. It is highly plausible that in the interesting range of energies, $D(E,V)$ will decrease in size as $E$ is reduced. However, the entropy of the system is still determined by the percolating cluster, at least at higher energies that correspond to temperatures much higher than the melting temperature $T_M$. Close to but still above $T_M$, another cluster $C(E,V)$ containing
ordered configurations relevant for the crystal state begins to form, and begins to compete with the disordered cluster $D(E, V)$ as far as their entropies are concerned. At $T_M$, there is a transition to the crystal, and the thermodynamics is now controlled by $C(E, V)$.

As we are interested in supercooled states, we will preclude the basins that determine $C(E, V)$. This gives rise to the restricted PF formalism to study metastability [14]. Consequently, we continue to consider $D(E, V)$ as we reduce the energy. At lower energies or temperatures, the cluster $D(E, V)$ will be fragmented enough so that the percolation ceases to occur mainly because the number of components has drastically decreased, and all we have are isolated components or clusters of components. The disconnected components will then force the system to undergo activation-assisted jumps between different basins and will force the system to undergo the dynamic glass transition. Thus, the picture strongly suggests a tantalizing possibility that the above percolation transition has direct relevance for the mode-coupling transition. We are working on this issue and hope to report soon in a separate publication.

B. Free energy distribution

The basins that contribute to the thermodynamics are enumerated by $N(\varphi, T, V)$. All these basins have the same equilibrium energy, entropy and the free energy, as discussed above. Other basins containing configurations of energy $E(T, V)$, but not satisfying the other conditions do not contribute, even though they may be infinitely many, as discussed above. Some of them may even have their free energies $\bar{\varphi}(T, V) < \varphi_0(T, V)$; they still will not determine the thermodynamics because the corresponding free energy $\bar{F}(T, V)$ due to basins with free energy $\bar{\varphi}(T, V)$ is higher than the equilibrium free energy $F(T, V)$ discussed above in (23). Such a possibility $(\varphi_2 = \bar{\varphi} < \varphi_0)$ has an interesting consequence. The probability for probing one of the nonequilibrium basins is

$$P_j(T, V) = \exp[-\mathcal{S} - \beta(\bar{\varphi} - \varphi_b)],$$

and is higher than the probability to be in an equilibrium basin; here, $\mathcal{S}$ is the equilibrium complexity $\mathcal{S}(\varphi_0, T, V)$. There is nothing wrong with it. Let $\exp[\mathcal{S}(\bar{\varphi}, T, V)]$ denote the number of nonequilibrium basins with the basin free energy $\bar{\varphi}$. Then, the probability $\bar{P}(T, V)$ to be in any of these basins is obtained by multiplying this number by $P_j(T, V)$ above, which yields

$$\bar{P}(T, V) = \exp[-\beta(\bar{F} - F)],$$

which surely vanishes for a macroscopic system since $F$ is the lowest free energy. Thus, we can neglect the nonequilibrium basins in thermodynamic considerations, even though they are important for studying transition rates from one state to another, which we discuss below.

C. Transitions among Basins

We have already argued that all equilibrium basins are equally probable; see (34). This is nothing but the Boltzmann hypothesis of microstates [1]; the only difference is that the microstates are now replaced by the basins, and the microstate energies $E$ are replaced by the basin free energies $\varphi$. Since there is no physical interactions between basins, each basin can be thought of as representing a ”microstate” of the system. Thus, the emergence of the principle of equiprobability of basins is not surprising. What is surprising is that this principle is valid even if we consider a restricted PF in which we disallow certain configurations (or basins) like those relevant for crystallization. Such a PF is used to study metastable states like supercooled liquids [3–5, 14]. Thus, the above principle gives rise to a ”restricted” ergodic behavior within the restricted PF formalism. With this analogy, we can now begin to understand the time-evolution of the system, since it is well-known [1] that the principle of equiprobability is equivalent to the principle of detailed balance or Liouville theorem: If states (or basins) $B_1$ and $B_2$ have the same (free) energy, then the probability $P_{12}$ per unit time of a transition from $B_1 \rightarrow B_2$ and the probability $P_{21}$ per unit time of the reverse transition from $B_2 \rightarrow B_1$ are the same:

$$P_{12} = P_{21}.$$ 

The rate at which the transition $B_1 \rightarrow B_2$ takes place is

$$\mathcal{R}_{12} = P_1 P_{12},$$

where $P_1$ is the probability that the system explores the basin $B_1$; we have suppressed the arguments $T, V$ for simplicity. It is clear that $\mathcal{R}_{12} = \mathcal{R}_{21}$.

It should be noted that $P_{ij}$ for transitions $B_i \rightarrow B_j$ need not all be the same for all choices of $i$ and $j$. Indeed, some of them may be zero. Assume that at a given instance, the system is probing a basin $B_1$, and has a very small probability of getting into some basin $B_0$, because there is only one pathway through intermediate (equilibrium and nonequilibrium) basins $B_2, B_3, B_3, \ldots$ to $B_0$. While there may be an appreciable probability for the transition $B_1 \rightarrow B_2, B_1 \rightarrow B_3$, etc. because of a large number of pathways connecting $B_1$ to $B_2, B_1$ to $B_3$, etc., the probability of transition $B_1$ to $B_0$ remains very small. This also implies that the probability of the reverse transition $B_0$ to $B_1$ is also small as there is only one path connecting $B_0$ to $B_1$. It may also happen that the probability of transition to other basins from $B_0$ is very small. This will mean not only that it is highly unlikely for the system to get into the basin $B_0$, but also for it to escape $B_0$. In no way does this violate the principle of equiprobability. What this situation corresponds to is this: once the system begins to probe the basin $B_0$, it stays there for a long time before escaping. The amount of time the system probes the basin $B_0$ is still the same as the amount of time it spends in any other
basins $B_1, B_2, B_3$, etc., which is what the principle of equiprobability implies [1].

The rate $\dot{P}_i$ at which $P_i$ changes with time is given by

$$\dot{P}_i \equiv \sum_j P_j P_{ji} - P_i \sum_j P_{ij},$$

where we must remember that $P_{ji} = P_{ij}$. In general, the transition probability $P_{ij}$ satisfies

$$P_{ij} \equiv 1 - \sum_{k \neq j} P_{ik}.$$  (43)

The situation in which $B_0$ has only a few escape routes to other basins becomes more probable as the temperature is reduced. The value of $P_{00j}$ depends, not on the free energy heights of the energy barriers but on their ratios with $T$. Thus, at low temperatures, $P_{00j}$ can be very small for two disjoint basin components. That does not mean that the system will be trapped in $B_0$, unless there are only a few basins (thermodynamically insignificant in number) in the sum in (43) so that $P_0 \equiv 1$. If there is a large number of basins (thermodynamically significant in number) in the sum in (43), $P_0 < 1$ and the system will be able to escape to some other basins. It is quite clear that the probability of staying in a given basin increases as $T$ is reduced, mainly because there are only a few basins left in the system at that temperature. This is the mechanism behind the glass transition.

To study the trapping of the system to a single basin $B_0$ at low temperatures, we can follow the standard idea of symmetry breaking in condensed matter and apply a symmetry breaking bias $\lambda_0(> 0)$ to make the free energy of $B_0$ lower than the free energies of other equiprobable basins: $F_0(T, V) = F(T, V) - \lambda_0$. This will single out the basin $B_0$ from all equiprobable basins. At the end of the calculation, we can take the limit $\lambda_0 \to 0$.

D. Equilibrium identifier Energy $\mathcal{E}(T, V)$

Let us introduce the mean identifier energy

$$\tilde{\mathcal{E}}(\varphi, T, V) = \frac{1}{\mathcal{N}(\varphi, T, V)} \sum_{j=1, N(\varphi, T, V)} \mathcal{E}_j(V)$$  (44)

over all basins with the same free energy $\varphi$. These need not be the equilibrium basins. Furthermore, they not all have the same $\mathcal{E}_j(V)$. Using (42) in (26), we can write

$$\mathcal{E}(T, V) = \sum_{j=1, N(\varphi)} \mathcal{E}_j(V) \exp[-S - \beta(\varphi_j - \varphi_b)].$$

Let $\exp[S(\varphi, T, V)]$ denote the number of basins with the basin free energy $\varphi$. Grouping basins according to their free energy $\tilde{\varphi}$, and introducing $\tilde{F}(\tilde{\varphi}, T, V) = \tilde{\varphi} - T S(\tilde{\varphi}, T, V)$, we can write

$$\mathcal{E}(T, V) = \sum_{\tilde{\varphi}} \tilde{\mathcal{E}}(\tilde{\varphi}, T, V) \exp[-\beta(\tilde{F} - F)].$$

Since $F$ is the lowest free energy corresponding to $\varphi_b$, we can replace the sum over $\tilde{\varphi}$ by the most dominant term corresponding to $\tilde{\varphi} = \varphi_b$, i.e. $\tilde{F} = F$. This finally gives

$$\mathcal{E}(T, V) = \tilde{\mathcal{E}}[\varphi_b(T, V), T, V].$$

The sum in (44) for $\tilde{\varphi} = \varphi_b$ is over the equilibrium basins counted in $\mathcal{N}(\varphi_b, T, V)$. The equilibrium identifier energy must be extensive. The range $\mathcal{R}(T)$ over which $\mathcal{E}_j$ varies in (44) will depend on the system, and it is conceivable that $\mathcal{R}(T)/N$ is not zero in the thermodynamic limit, as we discussed above. In this case, the free energy $f_j(T, V)$ will not be the same for all equilibrium basins. However, Goldstein [3] intuitively argues that $\mathcal{R}(T)/N$ should vanish for basin minima as the identifier, and that the basin minima have a sharp distribution about its equilibrium. If this is correct, it would imply that all equilibrium basins also have the same average minima in additions to the conditions in (S2). This will imply that all basins are identical in the thermodynamic sense (though not necessarily in the topological sense).

All we can say is that our analysis is completely oblivious of the basin minima or other identifier energies $\mathcal{E}_j$.

Going back to the modified PF in (27), we observe that as $\lambda \to 0$, there is no bias whether lower identifier energies are weighted more (\(\lambda > 0\)) or higher identifier energies (\(\lambda < 0\)) are weighted. However, there will in general be some topological restrictions. For example, basins with $E_{\lambda} > E(T, V)$ or $E^{\text{H}} < E(T, V)$ are not allowed, but this puts no strong restriction on the range $\mathcal{R}(T)$. For example, all basins with $E_{\lambda} < E(T, V)$ regardless of how low they are will contribute to $E_{\lambda}(T, V)$, as long as the corresponding basin free energy is equal to $\varphi_b(T, V)$. Thus, it is not clear whether $\mathcal{R}(T)/N$ is really zero in the thermodynamic limit.

E. Complexity as Free Energy?

The complexity appears in an additive fashion in the free energy, which suggests the identification of $\mathcal{N}(\varphi, T, V)$ as some kind of a configurational state PF $Z_{\text{CS}}(T, V)$ [think of $Z_{\text{CS}}(T, V)$ as the factor $Z_{\text{BM}}(T, V)$ in (4)], even though the former truly determines an entropic quantity $S(\varphi, T, V)$, called complexity; see (7).

Usually, the microcanonical entropy in statistical mechanics is a natural function of energy, and not temperature [1], whereas $\mathcal{N}(\varphi, T, V)$ is a function the temperature. Despite this, we now show that it is not proper to think of the above identification $Z_{\text{CS}}(T, V) \equiv \mathcal{N}(\varphi, T, V)$ for the following reason. The identification will yield the free energy $F_{\text{CS}}(T, V) \equiv -T \ln Z_{\text{CS}}(T, V) = -TS$, from which we can compute the corresponding entropy $[\partial F_{\text{CS}}(T, V)/\partial T]$, and energy $[E = F + TS]$

$$S_{\text{CS}}(T, V) = S + T \left( \frac{\partial S}{\partial T} \right)_V,$$

$$E_{\text{CS}}(T, V) = T^2 \left( \frac{\partial S}{\partial T} \right)_V.$$
We now use this in (23), and obtain
\[ F(T,V) = E_b(T,V) + E_{CS}(T,V) - T[S_b(T,V) + \overline{S}(T,V) + T \left( \frac{\partial \overline{S}}{\partial T} \right)_V]. \]

This form of the free energy will give for the energy the first two terms, which is not correct; see (39). Similarly, the quantity in the square rackets also is not the correct entropy of the system; see (7). Hence, complexity should not be considered as a free energy. Its proper identification is with the entropy. This justifies using the complexity as the entropy associated with configurational states. This entropy is neither the entropy \( S_{\text{CS}}(T,V) \) nor the entropy \( S_{\text{BI}}(T,V) \) due to any basin identifier. The entropy associated with the configurational states advocated by Goldstein truly represents the entropy associated with the basins of a given free energy \( \varphi \), and not a given BM energy. Moreover, the configurational states of Goldstein should be identified as the basins of a given free energy \( \varphi \).

F. Extension to NTP-Ensemble

For the NTP-ensemble, we need to integrate \( Z(T,V) \exp(-\beta PV) dV \); see the PF in (1), over the volume, so that the role of \( V \) in the above discussion is played by the equilibrium volume \( \overline{V}(T,P) \) and should be replaced by it. All the above formulas remain valid if we replace \( V \) by either \( P \) or \( \overline{V}(T,P) \) in all thermodynamic quantities. (It is for this reason that we have explicitly shown \( V \) in all the formulas above.) For example, the basin energy is represented as a function \( E_j(T,P) \) or \( E_j[T,\overline{V}(T,P)] \). The same is true of the basin free energy \( \varphi \), which now represents the Gibbs free energy. The complexity is to be treated as a function of \( \varphi, T, \) and \( P \) or \( \overline{V}(T,P) \).

The PE landscape is now defined in a \((3N + 2)\)-dimensional landscape space \( \Lambda_N \) in which \( V \) is added as an additional axis. The PE surface is now a \((3N + 1)\)-dimensional surface \( \Sigma \). Since the configuration space \( \Gamma(V) \) requires a particular volume \( V \) for its definition, we need to project \( \Sigma \) for a particular value of \( V \). Thus, we need to deal with the same sort of projection \( \Pi(V) \) in the configuration space as before. The slice \( d\Sigma \) also needs to be projected for a particular value of \( V \). Thus, we determines the number of configurations \( W(E,V) \) for a given \( E \), and \( V \). In equilibrium, corresponding to \( E, \) and \( V \) exist \( T, \) and \( P \) such that \( E(T,P) = E, \) and \( V(T,P) = V \). All the conclusions above remain valid.

G. Summary

In summary, we have investigated the landscape description at all temperatures, even though the picture was originally introduced by Goldstein as valid and useful only at low temperatures. We have succeeded in validating the picture at any temperature. Thus, the results we present here are not restricted to any particular temperature. We have shown that the basins represent the configurational states that were introduced by Goldstein. These basins and their free energy \( \varphi \) play the role of microstates and their energy \( E \) in the microcanonical ensemble, and are governed by a similar equiprobability principle, which extends the Boltzmann equiprobability principle for microstates. The corresponding entropy due to the number of basins of a given free energy is called the complexity [9], and correctly represents an entropy and not a free energy. We have shown that the entropy is a sum of complexity and intrabasin entropy. We also conclude that all equilibrium basins at a given temperature not only have the same equilibrium free energy \( \varphi_b(T,V) \), but also have the same energy \( E(T,V) \), and the same intrabasin entropy \( S_b(T,V) \). Because of the relevance of equilibrium basin identifiers in different temperature ranges, we have provided a procedure to express thermodynamic quantities as a function of equilibrium basin identifier energy \( E(T,V) \) since the equilibrium free energy does not explicitly depend on \( E(T,V) \). Our analysis provides justifications for two of the conjectures made by Goldstein but with slight modifications. The equiprobability theorem allows to draw some conjectural conclusions about the dynamics and the role of landscape projection components in the phase space. We discuss the percolation of basin projection components and speculate about the possible connection of the disappearance of percolation with the dynamic glass transition. This topic is being investigated at present and we hope to report on it in near future.

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The potential energy when two or more particles overlap is infinitely large. To avoid this infinity, we will assume that the centers of mass of two particles are not allowed to be less than some distance $d$. Let $E_d > 0$ be the potential energy between two particles at this distance. The maximum energy when all the particles are at a distance $d$ from each other is $N(N-1)E_d/2$, but such an event is very rare. Even the probability of having a large but finite numbers of particles being at a distance $d$ from each other is very small. Hence, we will assume that the highest allowed energy due to close proximity is $E_{CP} = cNE_d$, where $c$ is some small and non-zero constant. In this case, some of the basins may have $E_j^H = E_{CP}$. All other basins are expected to have their $E_j^H < E_{CP}$.

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