

Configurational States and Their Characterization in the Energy Landscape

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Abstract

Configurational states that are to be associated, according to Goldstein, with the basins in the potential energy landscape cannot be characterized by any particular basin identifiers such as the basin minima, the lowest barrier, the most probable energy barrier, etc., since the basin free energy turns out to be independent of the energies of these identifiers. Thus, our analysis utilizes basin free energies to characterize configurational states. When the basin identifier energies are monotonic, we can express the equilibrium basin free energy as a function of an equilibrium basin identifier energy, as we explain, but it is not necessarily unique.
It is well known that most supercooled liquids (SCL) become viscous when their configurational entropy becomes negligible as they are cooled, provided the corresponding crystal is not allowed to nucleate. 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 (PEL) picture using classical canonical ensemble \textsuperscript{1,2} to qualitatively discuss an interesting and sufficiently tractable scheme to study SCL and the glassy state by drawing attention to the potential energy basins that are expected to play a pivotal role in the thermodynamics of viscous fluids at low temperatures. The PE surface contains many local potential energy basins, each possessing a basin minimum (BM). The study paved the way to exploit PEL to study stationary SCL by the use of the partition function (PF) formalism. The stationary state is obtained under infinitely slow cooling of the disordered equilibrium liquid below the melting temperature \(T_M\). The basins have other points of interest such as the lowest energy barrier (LB) or the most probable energy barriers, i.e. the barriers with the highest population (MPB) that most probably play an important role in crossover dynamics or diffusion, as the temperature is raised. We will collectively call these basin points of interest basin identifiers. Goldstein provided a qualitative description of the nature of the resulting landscape created by the distribution of basins and their minima, and drew attention to the idea of configurational states, which should be associated with individual basins and should change with the temperature \(T\). Instead of being determined by the particular topology of the basin, the configurational state of the system associated with that particular basin, according to Goldstein, is uniquely specified only by the potential energy \(\mathcal{E}\) of the basin minimum. This will certainly make sense if the equilibrium value \(\mathcal{E} = \mathcal{E}(T)\) of \(\mathcal{E}\) is in one-to-one correspondence with (i.e., is a monotonic function of) the temperature \(T\). We wish to emphasize that throughout this work, we are only interested in non-equilibrium temperatures.

As we will see below, there is no thermodynamic requirement for \(\mathcal{E}(T)\) to be monotonic. Even if \(\mathcal{E}(T)\) is monotonic, it is expressing thermodynamic properties as a function of \(\mathcal{E}(T)\) over a wide range of temperature an oversimplification, since it makes the shape and topology of the basins irrelevant? For example, if we consider a particular basin, then its energy changes with \(T\), but the basin minimum energy remains unaffected by \(T\). Similarly, the free energy also changes as the system moves from one basin to another at the same temperature. The BM energy \(\mathcal{E}\) has no guarantee to remain the same. This change in \(\mathcal{E}\) is certainly not going to be reflected in \(\mathcal{E}(T)\). Thus, we expect not only the equilibrium \(\mathcal{E}(T)\) but all equilibrium quantities to have separate intrabasin and interbasin contributions. Indeed, this happens as we will see here [see \(\bullet\) below]. We find that the equilibrium value of every thermodynamic quantity including \(\mathcal{E}\) is a function not only of \(T\), but also of the basin free energy. Only at low temperatures do we expect the latter dependence on the free energy to become weak as assumed by Goldstein. In that case, the use of \(\mathcal{E}\) may lead to erroneous description if care is not exercised. What about other points like LB and MPB in the basins? Will they play a more important role at higher temperatures? Is there a thermodynamic basis for their importance?

It is obvious that the shape and topology uniquely determine the free energy of the basins, which then uniquely determine the thermodynamics of the viscous fluid. Should we not describe configurational states by specifying the basin free energy? The latter is certainly monotonic in \(T\). We note in this regard that, based on an analogy with spin glasses, the use of basin free energy in place of the BM energy, as originally advocated by Goldstein, has been proposed \[3, 4, 5, 6\]. An alternate approach is to use the free energy landscape \[7\] and has been applied, for example, to dense hard sphere system \[8\] to study glassy behavior. Here, we are only interested in the potential energy landscape. The use of PEL has now become common in many disparate fields like glasses, proteins and clusters \[9\], and has established itself as an important thermodynamic approach in theoretical physics. Thus, it is highly desirable to answer the above questions. It is this desire that has motivated this investigation.

We briefly review the basics of the PF formulation in statistical mechanics \[10\] as some of the steps in the evaluation of the PF are going to be crucial in our discussion here. The PF \(Z(T)\) is a sum of the Boltzmann weight \(\exp(-\beta E_n)\) for each configuration of energy \(E_n\)

\[
Z(T) = \sum_n e^{-\beta E_n},
\]

(1)

Here \(n\) indexes the configurations of the system. However, as we can change the value of \(n\) associated with a configuration at will by relabeling it, the index \(n\) is not unique and, therefore, its possible values for equilibrium configurations are not very useful for thermodynamic description. Therefore, we need to relate \(n\) to a unique thermodynamic property of all configurations, and not just the equilibrium configurations. The property must be such that its equilibrium value is a monotonic function of \(T\), so that it can be used in place of \(T\) if we so wish. It is not hard to identify such a property. Since each configuration has a unique energy, which is a thermodynamic quantity, we can use the energy \(E_n\) in place of \(n\) as the summation index. As the energy of interactions \(E_n\) is coupled to the inverse temperature \(\beta\), see \[11\], the equilibrium energy

\[
\overline{E} \equiv E(T) \equiv \sum_n E_n e^{-\beta E_n} / Z(T)
\]
Thus, the first step is to rewrite the PF in (1) as

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

(2)

where $W(E)$ represents the number of configurations of energy $E$ and defines the microcanonical entropy $S(E) \equiv \ln W(E)$. The sum in $Z(T)$ at a fixed $T$ is over all allowed energies $E$ and, by construction, each summand is also a function of $E$. These energies and, therefore, $S(E)$ do not depend on $T$. The second step in the evaluation is to recognize that the value of $Z(T)$ for a macroscopic system, which is what we consider here, is determined by the dominant term in the sum. The dominant term corresponds to the equilibrium energy $E$ at which the summand in (2) is maximum. Thus, $Z(T) \approx W(E_0) e^{-\beta E_0}$. It is the presence of $W(E)$ in (2) that makes the summand strongly peaked at $E_0$. The determination of $E_0$ for a macroscopic system is simplified by noting that $E_0$ is almost a continuous variable for a macroscopic system. In terms of $S(E)$, $E$ is given by the location of the minimum of the free energy function $F(T, E) = E - TS(E)$ at fixed $T$. In equilibrium, the canonical entropy $S(T) \equiv S(E)$ and free energy $F(T) \equiv F(T, E) = E(T) - TS(T)$ become functions only of $T$. The conditions for the minimum are

$$\left. \frac{\partial S(E)}{\partial E} \right|_{E=E(T)} = \beta, \quad \partial S(T)/\partial T > 0,$$

(3)

which are always satisfied in equilibrium.

At a given temperature $T$, only those configurations that have the energy $E = E_0$ (or within a narrow width around it, depending on the heat capacity; we will neglect this width here) determine the thermodynamics through the entropy $S(T)$. All energies other than $E_0$ and, therefore, all configurations not included in $W(E)$ are irrelevant at $T$. Thus, thermodynamics is highly selective. We will call configurations with $E = E_0$ equilibrium configurations to distinguish them from all configurations. All thermodynamic quantities related to equilibrium configurations will be similarly called equilibrium quantities to distinguish them from quantities related to general configurations that may not be equilibrium ones. In the following, we will make this distinction carefully.

As said above, the equilibrium values of $E$ are strongly peaked about $E_0$; all these configurations have the same minimum free energy $F(T)$. These configurations belong to different basins with different BM energies. Therefore, $E_0$ at a given temperature must be independent of $\mathcal{E}$. However, there is no guarantee that the the equilibrium values of $\mathcal{E}$ are also strongly peaked about $E_0$. In other words, there is requirement that equilibrium configurations all belong to basins having their minima that are strongly peaked about $E_0$. It is certainly possible for equilibrium configurations to belong to different basins that have their minima at different energies, but still correspond to the same free energy $F(T)$ because of the shape of the basins. In this case, it does not seem reasonable to classify equilibrium configurations only by the minima of the basins they belong to. We must also use the basin free energy in addition to the BM energies for this purpose as discussed above. However, it appears highly plausible that it can be done at low temperatures as originally proposed by Goldstein since the basin free energies are close to the BM energies in values.

In his analysis, Goldstein has considered basin minima as the basin identifier, and has listed two conjectures that were common in the field at the time: the basin PF $z_b(T)$ is (i) independent of the basin’s minimum energy $\mathcal{E}$, and (ii) insensitive to the basins being explored. Utilizing these assumptions, Goldstein has expressed the PF as a product of the basin and BM PF’s

$$Z(T) = z_b(T) Z_{BM}(T);$$

(4)

here $z_b$ for a given basin is defined by considering shifted energies $E - \mathcal{E}$ with respect to the minimum energy $\mathcal{E}$ of that basin; see also Schulz. Goldstein has emphasized that basin anharmonicity or the curvature at its minimum may be very important. These are included in $z_b$, so that it is determined by the entire basin topology. According to Goldstein, all equilibrium basins have the same equilibrium basin free energy $f_b(T) \equiv -T \ln z_b$. The BM-PF is defined as

$$Z_{BM}(T) = \sum_\mathcal{E} N_{BM}(\mathcal{E}) e^{-\beta \mathcal{E}}.$$  

(5)

Here, $N_{BM}(\mathcal{E})$ represents the number of basins whose BM are at energy $\mathcal{E}$. The equilibrium BM energy $\bar{\mathcal{E}} = \mathcal{E}(T)$ is the value of $\mathcal{E}$ at which the summand in (5) is maximum. The conditions for the maximum in terms of the BM entropy $S_{BM}(\mathcal{E}) \equiv \ln N_{BM}(\mathcal{E})$ are given by

$$\left. \frac{\partial S_{BM}(\mathcal{E})}{\partial \mathcal{E}} \right|_{\mathcal{E}=\bar{\mathcal{E}}} = \beta, \quad \partial \bar{\mathcal{E}}/\partial T > 0,$$

(6)
which are the standard conditions of equilibrium; compare with [3]. It is clear that the BM description proposed by Goldstein ensures that $\mathcal{E}$ is a monotonic increasing function of $T$. Since his approximation is expected to be good at low temperatures, we expect $\mathcal{E}$ to monotonic increasing there. But we will see below that it need not be true at all temperatures, thereby limiting the usefulness of the BM-description to which we now turn.

**BM Picture.** We take BM’s as basin identifiers, but the discussion is easily extended to LB’s or MPB’s, or other basin identifiers. The PEL is a union of disjoint basins. A basin is indexed by $j$, and the lowest and highest basin energies are denoted by $E_j$, and $\mathcal{E}_j$, respectively, so that the basin does not exist outside the energy range $\Delta E = (E_j, \mathcal{E}_j)$. Since PEL does not depend on $T$, $E_j$ and $\mathcal{E}_j$ do not depend on $T$. Let $W_j(E)$ ($E \in \Delta_j E$) represent the number of distinct configurations of energy $E$ in the $j$-th basin and introduce the entropy $S_j(E) \equiv \ln W_j(E)$. It is obvious that $W_j(E)$ is determined by the basin topology, which in turn is determined by the the interaction energies in the system. Let $W_j(E)$ attain its maximum at $E_{jm}$ and introduce $\Delta_{jm} E \equiv (\mathcal{E}_j, E_{jm})$. We now introduce the shifted PF

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

of the $j$-th basin. Let $E_j(T), S_j(T)$ be the average basin energy and entropy, so that $f_j(T) \equiv -T \ln z_j(T) = E_j(T) - E_j - TS_j(T)$. The former condition is the price paid to make $E_j(T)$ represent the basin’s shifted free energy. Of course, the corresponding $E_j(T)$ have to be close in the configuration space. The number of basins in a class $\lambda$ (denoted by $\mathcal{B}_\lambda$, indexed by $\lambda$, so that all basins in a class have the same BM energy $E = \mathcal{E}_\lambda$. The basins in a class do not have to be close in the configuration space. The number of basins in $\mathcal{B}_\lambda$ is $N_{BM}(\mathcal{E}_\lambda)$, and the corresponding BM entropy is $S_{BM}(\mathcal{E}_\lambda) \equiv \ln N_{BM}(\mathcal{E}_\lambda)$. The introduction of $N_{BM}(\mathcal{E}_\lambda)$ and $S_{BM}(\mathcal{E}_\lambda)$ requires that they have a one-to-one relationship with $\mathcal{E}_\lambda$. Let

$$Z_\lambda(T) \equiv \sum_{j \in j(\lambda)} z_j(T) \quad z_\lambda \equiv Z_\lambda(T)/N_{BM}(E_\lambda),$$

denote the shifted and the mean (per basin) shifted $\mathcal{B}_\lambda$-PF, respectively, so that

$$Z(T) \equiv \sum_\lambda e^{-\beta \mathcal{E}_\lambda} Z_\lambda(T) \equiv \sum_\lambda e^{-\beta \mathcal{E}_\lambda + S_{BM}(\mathcal{E}_\lambda)} z_\lambda(T), \quad (10a)$$

$$\mathcal{E}(T) \equiv \sum_j \mathcal{E}_j e^{-\beta \mathcal{E}_j} z_j(T)/Z(T) \equiv \sum_\lambda \mathcal{E}_\lambda e^{-\beta \mathcal{E}_\lambda} Z_\lambda(T)/Z(T). \quad (10b)$$

Here, $\mathcal{E} = \mathcal{E}(T)$ represents the equilibrium BM energy. The equilibrium free energy, entropy and energy are $F(T) = -T \ln Z(T)$, $S(T) = -\partial F/\partial T$ and $E(T) = F(T) + TS(T)$, respectively.

At a given $T$, the probability $\text{Pr}(T | \mathcal{B}_\lambda)$ that the system will probe the BC $\mathcal{B}_\lambda$, i.e., any of the basins in $\mathcal{B}_\lambda$ is

$$\text{Pr}(T | \mathcal{B}_\lambda) = e^{-\beta \mathcal{E}_\lambda} Z_\lambda(T)/Z(T). \quad (11)$$

On the other hand, the probability that the system will explore a particular basin $j$ among all the basins is

$$\text{Pr}(T | j) = e^{-\beta \mathcal{E}_j} z_j(T)/Z(T), \quad (12)$$

whereas the conditional probability that the system explores the basin $j$, given that the system is confined to the BC $\mathcal{B}_\lambda$, is

$$p_j(T | \lambda) = z_j(T)/Z_\lambda(T). \quad (13)$$

These probability distributions can be used directly to evaluate various entropies by using the Gibbs definition of the entropy as minus the mean logarithm of the probability distribution

$$S = -\langle \ln w \rangle, \quad (14)$$
where \( w \) is one of the probability distributions above. For example, the equilibrium entropy \( S(T) \) is obtained by considering the distribution in (12):

\[
S(T) = - \sum_j \Pr(T \mid j) \ln \Pr(T \mid j),
\]

(15)

The entropy \( \overline{S}(T) \) due to the number of different equilibrium BC’s, and the entropy \( \overline{S}_\lambda(T) \) due to basins within a BC are similarly given by

\[
\overline{S}(T) = - \sum_{\lambda} \Pr(T \mid B_{\lambda}) \ln \Pr(T \mid B_{\lambda}),
\]

(16)

\[
\overline{S}_\lambda(T) = - \sum_{j \in \lambda} p_j(T \mid \lambda) \ln p_j(T \mid \lambda).
\]

(17)

It is easy to see that the temperature coefficient \( \partial \overline{S} / \partial T \) is given by

\[
T^2 \partial \overline{S} / \partial T = \sum_{j=1}^{N_B} \Delta \mathcal{E}_j(T) \Delta \mathcal{E}_j(T) \Pr(T \mid j),
\]

(18)

where \( \Delta \mathcal{E}_j(T) \equiv \mathcal{E}_j - \overline{\mathcal{E}}, \Delta \mathcal{E}_j(T) \equiv \mathcal{E}_j(T) - E(T), \) and \( N_B \) is the number of basins. The derivative is a cross-correlation between two fluctuations, \( \Delta \mathcal{E}_j(T) \) and \( \Delta \mathcal{E}_j(T, V) \). Since cross-correlations do not usually have a fixed sign, there is no theoretical reason for \( \overline{\mathcal{E}} \) to be a monotonic increasing function of \( T \). This does not mean that the temperature coefficient cannot be positive for many physical systems in a certain temperature range. The same argument also works for other equilibrium identifier energies.

The sum over \( \lambda \) in (10) is over different basin classes, and the summand is also uniquely determined by each class. However, the index \( \lambda \) is not a unique labeling. Therefore, we need to associate with each class a unique thermodynamic class property. We also need to make sure that its equilibrium value is monotonic in \( T \). Thus, our task is to find a basin quantity that is not only a unique property of each class, but also determines the summand in (10). One of the simplest choices is to take the basin minima \( \mathcal{E} \) as the basin quantity for the simple reason that each BC has a uniquely BM energy \( \mathcal{E}_\lambda \), and it also appears in the summand in (10) provided we take \( z_\lambda \) to depend explicitly on \( \mathcal{E}_\lambda \) in addition to \( T : z_\lambda = z_\lambda(\mathcal{E}_\lambda, T) \). This contradicts the assumption by Goldstein [2]. However, this is a common choice; see [13]. If the interest is to study high temperatures near the dynamic crossover, one might take the LB-energy \( \mathcal{E}_{j, \text{LB}} \) of the \( j \)-th basin as the quantity of interest. In this case, one would group basins not by the their BM energies, by their LB energies, so that all basins in the BC \( \lambda \) have their LB at \( \mathcal{E}_{j, \text{LB}} \). Similarly, one can take the MPB-energy \( \mathcal{E}_{j, \text{MPB}} \) or some other special energy of the \( j \)-th basin as the quantity of interest. The analysis in all these cases would be carried out in the same manner as the analysis we carry out here for the BM picture, and would not be pursued further except for a few remarks later.

**Common Assumption.** The assumption \( z_\lambda = z_\lambda(\mathcal{E}_\lambda, T) \) as a function of two different variables \( T \), and \( \mathcal{E}_\lambda \) makes the summand an explicit function of \( \mathcal{E}_\lambda \). Note that \( \mathcal{E}_\lambda \) in the summand in (10) is a temperature-independent quantity. Let us follow the consequence of this assumption. Let the mean basin free energy resulting from the mean basin PF \( z_\lambda \) for the basin class \( B_{\lambda} \), and the mean basin entropy be \( f(\mathcal{E}_\lambda, T) = -T \ln z_\lambda(\mathcal{E}_\lambda, T) \), and \( S(\mathcal{E}_\lambda, T) = -[\partial f(\mathcal{E}_\lambda, T) / \partial T]_{\mathcal{E}_\lambda} \), respectively. The mean basin free energy \( f(\mathcal{E}_\lambda, T) = \mathcal{E}_\lambda(T) - \mathcal{E}_\lambda - T S(\mathcal{E}_\lambda, T) \) is obviously obtained by minimizing the free energy function \( f(\mathcal{E}_\lambda, E, T) = E - \mathcal{E}_\lambda - T S(\mathcal{E}_\lambda, E) \) with respect to \( E \) at constant \( T \) and \( \mathcal{E}_\lambda \). Here, \( S(\mathcal{E}_\lambda, E) \equiv S(\mathcal{E}_\lambda) - S_{\text{BM}}(\mathcal{E}_\lambda) \), and \( \exp[S(\mathcal{E}_\lambda)] \) represents the number of configurations of energy \( E \) that belong to \( B_{\lambda} \). The condition for the minimum is \( \partial S(\mathcal{E}_\lambda, E) / \partial \mathcal{E}_\lambda = \beta \) at \( E = \mathcal{E}_\lambda(T) \), which determines \( f(\mathcal{E}_\lambda, T) = E(\mathcal{E}_\lambda, T) - \mathcal{E}_\lambda - T S(\mathcal{E}_\lambda, T) \); here, \( S(\mathcal{E}_\lambda, T) = S(\mathcal{E}_\lambda, E(\mathcal{E}_\lambda, T)) \).

The sum over the index \( \lambda \) is now replaced by the BM variable \( \mathcal{E} = \mathcal{E} \). Because of the assumed \( \mathcal{E} \)-dependence, the general summand in (10) becomes an explicit function of \( \mathcal{E} \), and we can minimize the corresponding free energy function \( F_B(\mathcal{E}, T) \equiv \mathcal{E} + f(\mathcal{E}, T) - T S_{BM}(\mathcal{E}) \) with respect to \( \mathcal{E} \) at fixed \( T \) to determine \( Z(T) \) for a macroscopic system. The minimum of \( F_B(\mathcal{E}, T) \) is located by the condition \( \partial F_B(\mathcal{E}, T) / \partial \mathcal{E} \mid T = 0 \). This condition is satisfied at the equilibrium BM-energy \( \mathcal{E} = \mathcal{E}(T) = \mathcal{E}(T) \), see (10). It is also equivalently given by the solution of

\[
[\partial S_{BM}(\mathcal{E}) / \partial \mathcal{E}]_{\mathcal{E} = \mathcal{E}} = \beta \{ 1 + [(\partial f(\mathcal{E}, T) / \partial \mathcal{E})]_{\mathcal{E} = \mathcal{E}} \},
\]

(19)

and determines the equilibrium free energy \( F(T) = F_B(\mathcal{E}, T) \) and the BM-entropy \( S_{BM}(T) \equiv S_{BM}(\mathcal{E}) \). The solution of (10) yields \( \mathcal{E} = \mathcal{E}(T) \) as a function of a single variable \( T \). The equilibrium mean basin free energy and entropy are \( f_b(T) = f(\mathcal{E}, T) \) and \( S_b(T) = S(\mathcal{E}, T) \), respectively. It is easy to see that the form of the equilibrium free energy
\[ F_B(T) = f(\overline{E}, T) + \mathcal{E}(T) - TS_{BM}(\overline{E}) \] is the same as the free energy obtained by Goldstein in [4], except that the equations determining the equilibrium BM-energy are different; compare [10] and [14]. The two conditions become identical if \( f \) is taken to be independent of \( \overline{E} \), as was assumed by Goldstein.

Let us assume that \( \overline{E} = \mathcal{E}(T) \) is a monotonic function of \( T \), so that we can invert it to express \( T = T(\overline{E}) \), which can be used to express all \( T \)-dependent quantities like \( f_0(T), F(T), S_{BM}(T) \), etc. as functions of the equilibrium BM-energy \( \overline{E} \). We can also express \( f(\mathcal{E}, T) \) as a function of \( \mathcal{E} \) and \( \overline{E} \). All this means is that \( T \) and \( \overline{E} \) are equivalent. The equilibrium free energy \( f_0(\overline{E}) = f_0[T(\overline{E})] \) is a single-variable function of \( \overline{E} \) and says nothing uniquely about the \( \mathcal{E} \)-dependence in the two-variable function \( f(\mathcal{E}, T) \). This is most clearly seen in the Goldstein's scenario. While \( f_0(T) \) is independent of \( \mathcal{E} \), we can still express \( f_0(T) \) as \( f_0(\overline{E}) \). To conclude that \( f_0(T) \) is a two variable function having an additional \( \mathcal{E} \)-dependence would be a wrong conclusion. A similar inversion can be carried out in terms of the average LB-energy \( \mathcal{E}^{LB}_j(T) \) so that all quantities that depend on \( T \) can be expressed as a function of \( \mathcal{E}^{LB}_j(T) \), which suggests that there is nothing unique in the choice of BM energies as the thermodynamic quantity to replace the sum over \( \lambda \).

In the above analysis, we have only considered one \((\partial F_B(\mathcal{E}, T)/\partial \mathcal{E})_T = 0\) of the two conditions needed for the free energy minimization. The other condition is that the curvature of the free energy at the minimum be positive: \([\partial^2 F_B(\mathcal{E}, T)/\partial \mathcal{E}^2]_T > 0\). This issue has been investigated elsewhere [14], and will not be pursued here.

**Current Analysis.** We now proceed to prove our central result that \( \mathcal{E}_\lambda \) (or any other basin identifiers) cannot be the choice of the thermodynamic quantity to replace the sum over \( \lambda \) for two different reasons that will be discussed below. We observe that \( W(E) \) is a sum over various basins containing the energy \( E: W(E) = \sum_{j:E \in \Delta_j} W_J(E) \). We also observe that even for basins in a single BC \( \mathcal{B}_\lambda \), \( z_J(T) \) need not be equal.

1. **Evaluating \( z_J(T) \).** We first prove one of the assumptions by Goldstein [2] that \( z_J \) cannot depend explicitly on the BM energy \( \mathcal{E}_j \), see [7], though it most certainly depends on the shape of the basin, i.e. on \( j \). For example, the basin curvature and not \( \mathcal{E}_j \) determines the vibrational frequencies (including anharmonicity) which, in turn, determine the free energy \( f_j(T) \equiv -T \ln z_j(T) \) in the harmonic approximation. The latter is measured with respect to \( \mathcal{E}_j \), so it must be independent of \( \mathcal{E}_j \).

To be convinced that this is most certainly correct, consider two basins \( j = 1 \) and \( 2 \) that are identical in all respects (shape and topology), but have different BM energies, which we assume satisfy \( \mathcal{E}_1 < \mathcal{E}_2 \). Let us introduce \( \delta E = E - \mathcal{E}_1 \). Let \( W_j'(\delta E), S_j'(\delta E) = \ln W_j(\delta E) \) denote the number of, and entropy due to configurations of energy at a height \( \delta E \) above the basin minimum \( \mathcal{E}_j \) in the \( j \)-th basin. It is obvious that

\[
W_j'(\delta E) = W_j(E).
\] (20)

Now, for \( \delta_1 E = \delta_2 E = \delta E \), it is clear that \( S_j'(\delta E) = S_j'(\delta E) \) for the two identical basins, from which it immediately follows that \( \partial S_j'(\delta E)/\partial \delta E = \partial S_j'(\delta E)/\partial \delta E = \beta \). The free energies of the two basins are given in terms of the same average energy height \( \mathcal{E}(T) = \mathcal{E}_j(T) - \mathcal{E}_j \), where \( E_j(T) \) is the average basin energy in the \( j \)-th basin, and the same entropy \( S_j'(\delta E(T)) = S_j'(\delta E(T)) \):

\[
f_j(T) = \delta E(T) - TS_j'(\delta E(T)) = E_j(T) - \mathcal{E}_j - TS_j(T),
\]

and are equal, as expected, after we use [20]. Here, \( S_j(T) \) is the canonical basin entropy in the \( j \)-th basin. We can also check the veracity of the free energy equality by directly evaluating the shifted PF in [7]. We will not do this as it is trivial. The extension to many topologically identical basins is trivial. Thus, we conclude that the free energies \( f_j(T) \) do not depend on the BM energies \( \mathcal{E}_j \).

Indeed, a very general but direct proof can be given that the basin PF \( z_j(T) \) cannot depend on its BM energy \( \mathcal{E}_j \). Thus, the corresponding basin entropy \( S_j(T) \) is also independent of \( \mathcal{E}_j \). For this, let us shift all energies \( E \rightarrow E' \equiv E - C \) by some constant \( C \) in [7]. The number \( W_j(E) \) of states, all having the same energy \( E \), remains unchanged under the shift by \( C: W_j'(E) \rightarrow W_j'(E') = W_j(E) \); compare with [20]. Thus, \( z_j \) transforms under the shift as \( z_j(T) \rightarrow \sum_{E'} W_j'(E') e^{-\beta(E'-\mathcal{E}_j)} \), see [7], and remains unchanged for any arbitrary \( C \), including \( C = \mathcal{E}_j, \mathcal{E}_j^B \), or \( \mathcal{E}_j^{MPB} \) corresponding to the \( j \)-th basin.

This central result requires adopting a different approach than the above for the PF-evaluation, which we present below.

For a macroscopic system, \( z_j \) is determined by the maximum summand in [7] corresponding to \( E = \overline{E}_j = E_j(T) \in \Delta_j E \). In terms of the free energy function \( \varphi_j(E, T) \equiv E - TS_j(E) \), the energy \( \overline{E}_j \) is determined by \((\partial \varphi_j/\partial E)_T = 0\). As usual, this condition yields

\[
(\partial S_j(E)/\partial E)_{E=\overline{E}_j} = \beta, \quad \partial E_j(T)/\partial T > 0, \quad \overline{E}_j \in \Delta_j m E;
\] (21)

the restriction on the allowed values of \( \overline{E}_j \) ensures that we are only considering non-negative \( \beta \). Over this temperature range, \( S_j(T) = S_j(\overline{E}_j) \) and \( E_j(T) \) are monotonic increasing. On the other hand, the shifted free energy of the basin
is \( f_j(T) = E_j(T) - E_j - TS_j(T) \) is monotonic decreasing since \( S_j(T) = -\left[ \frac{\partial f_j(T)}{\partial T} \right]_{E_j} \geq 0 \). Since there is no \( E_j \)-dependence in \( f_j(T) \), as we have argued above, there is no need to show that the derivative \( \frac{\partial f_j(T)}{\partial T} \) at fixed \( E_j \).

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 \( T \) will be usually different not only from each other, but also from \( E(T) \) that appears in \( \phi \). In this sense, all basins are independent at this step of the analysis as they all do not represent equilibrium configurations. By the last step of the analysis, only equilibrium basins will survive for which \( E_j(T) = E(T) \).

2. Evaluating \( Z(\lambda) \). As shown above, \( z_j(T) \) is not a function of \( E \). We now need to replace the summation over \( j \) in \( \phi \) by a suitable thermodynamic quantity. There are various choices for the sum in \( \phi \) like the basin free energy \( f_j(T) \), the basin energy \( E_j(T) \), or the basin entropy \( S_j(T) \), all equally good. All these quantities are monotonic in \( T \). We will choose \( f_j(T) \) in the following to be the thermodynamic quantity to replace the sum over the index \( j \). As the basins in \( B_\lambda \) do not all have the same free energy, we classify each basin in \( \phi \) according to its free energy \( f \) at a given temperature \( T \). Let \( N_\lambda(f, T) \) denote the number of basins of free energy \( f \) at a given \( T \) in \( B_\lambda \), and let \( S_\lambda(f, T) \equiv \ln N_\lambda(f, T) \) be the corresponding entropy. For a macroscopic system at a given fixed \( T \), \( Z_\lambda \) is dominated by the basins in \( B_\lambda \) for which \( F_\lambda(f, T) \equiv f(T) - TS_\lambda(f, T) \) is minimum as a function of \( f \) at fixed \( T \), the conditions for which \( \lambda \) are \( \lambda \) and \( \lambda \) are \( \lambda \) and which also uniquely determine the summand. For this we proceed in a standard manner as follows. Let \( N(F, T) \) denote the number of BC’s at a given \( T \) with the same \( F = E_\lambda + F_\lambda(T) \), where \( F \) is the unshifted BC free energy now with respect to the zero of \( E \). Since \( F \) for different basin classes are now measured from the same common point \( E = 0 \), it is clear that we can consider all those BC’s that have the same free energy \( F \) at some \( T \), then this \( F \) no longer depends on the individual BC energy \( E \). The PF \( Z \) is dominated by the BC’s for which \( F - TS \) is minimum over \( F \); here \( S(F, T) \equiv \ln N(F, T) \). One of the conditions for this minimum at \( F \) is

\[
[(\partial S/\partial F)_T]_{F=T} = \beta,
\]

as expected. Hence, we finally conclude that the free energy of the system is given by

\[
F(T) \equiv -T \ln Z \equiv F - T\bar{S};
\]

here, \( \bar{S}(F, T) \equiv S(F, T) \). It should be obvious at this point that the dominant contribution in \( \phi \) will usually mix BC’s with different \( E \).

The equilibrium free energy is the sum of three terms: \( F(T) = \varphi_b(T) - TS_{BC}(T) - T\bar{S}(T) \), where \( S_{BC} \) denotes the equilibrium basin class entropy and \( \varphi_b(T) \) the equilibrium basin free energy. Expressing \( \varphi_b(T) = E_b(T) - TS_b(T) \), we immediately see that

\[
S(T) = S_b(T) + S_{BC}(T) + \bar{S}(T).
\]
Introducing \( F_\lambda = \mathcal{E}_\lambda + F_\lambda(T) \), we can express the probability \( \Pr(T | B_\lambda) \), see (11), that the system will explore \( B_\lambda \) in terms of \( F_\lambda \),

\[
\Pr(T | B_\lambda) = e^{-\beta[F_\lambda - F]}. \tag{27}
\]

It is easy to check that using the above probability in (16), we obtain the above entropy \( \mathcal{S}(T) \). In terms of the above probability in (27), the equilibrium BM energy, see (10b), is expressed as follows:

\[
\mathcal{E}(T) = \sum_\lambda \mathcal{E}_\lambda \Pr(T | B_\lambda). \tag{28}
\]

Thus, unless \( \mathcal{S}(T) = 0 \), so that there is only one BC, the equilibrium BM energy \( \mathcal{E}(T) \) is not given by the BM energy of a single BC. In other word, the system will usually explore many basin classes of different BM energies, unless \( \mathcal{S}(T) = 0 \), it is expected that \( \mathcal{S}(T) \) vanishes at low temperatures. Thus, the use of BM’s makes perfect sense at low temperatures as Goldstein had argued [1, 2]. At higher temperatures, many BC’s with different \( \mathcal{E}_\lambda \) are involved in (28).

The last prediction is different from the BM approach in which the equilibrium basins all have the same average BM energy \( \mathcal{E}(T) \). Let us try to understand this point carefully. Let us group the BC’s according to their free energy identifiers at a given temperature. If \( \mathcal{E}(T) \) is expressed as a function of \( \beta(T) \), \( \mathcal{E}(T) \) can be expressed as a function of \( \lambda(T) \) = \( \mathcal{E}(T) \).

Following a similar analysis that we have carried out here using BM as the point of interest, we can derive a similar relation like (31) for the above two equilibrium energies. We will not do this here. By comparing the equilibrium energy \( \mathcal{E}(T) \) with the equilibrium values in (33), we can draw conclusions about the importance of various basin identifiers at a given temperature.

The landscape analysis developed here does not involve the equilibrium BM energy \( \mathcal{E} \), because \( \mathcal{E}_j \) are not the natural energies that appear in the PF. Despite this, it is possible to express thermodynamic quantities in terms of \( \mathcal{E} \) under certain conditions that we elucidate below. The equilibrium basins at a given temperature form a subset of all basins and determine the equilibrium thermodynamics. If \( \mathcal{E}(T) \) is monotonic in \( T \), we can invert the relation \( \mathcal{E}(T) \) as before: \( T = T(\mathcal{E}) \). Thus, we can express any function of \( T \) as a function of \( \mathcal{E} \). For example, the equilibrium basin free energy \( f_j(T) \) can be expressed as a function of \( \mathcal{E} = \mathcal{E}(T) \). This is one way to express the equilibrium free energy as a function of \( \mathcal{E}(T) \). There are other ways to do this, as we will discuss below.
We can use $E(T)$ at a given $T$ to select only the equilibrium basins whose average energy is $E(T)$. This is precisely what is done when equilibrium configurations are generated in simulations carried out at a fixed $T$ without any consideration of the basins. From these equilibrium configurations, equilibrium basins can be identified. These basins also appear in and determine $\mathcal{F}$. But simulations can also provide information about whether there are many different BC’s that contribute to $\mathcal{F}$. (Unfortunately, to the best of our knowledge, simulations carried on finite-size systems have not been used to unequivocally answer whether the spread in the allowed values of $\mathcal{E}$ are thermodynamically significant are not.) The equilibrium free energy $f(T)$ of these basins will depend on the average topology of the basins. For example, in the harmonic approximation, $f(T)$ will be determined by the curvature (given by the set $\nu$ of vibrational frequencies) at the BM, and should be expressed as a function $f(\nu, T)$. These equilibrium frequencies will change with $T$. Being a function of $T$, they can also be expressed as a function of $\mathcal{E}$ as discussed above. Thus, the equilibrium basin free energy can be expressed as a function $f(\mathcal{E}, T)$. This provides us with another way to express $f(T)$ as a function of $\mathcal{E}$. Such a dependence on $\mathcal{E}$ of the equilibrium basin free energy should not be confused with any explicit $\mathcal{E}$-dependence of $z_j(T)$ in (7), or $z_\lambda(T)$ in (10a), since such a dependence has been shown not to exist. The free energy in (19) is not this equilibrium free energy in its new form. Moreover, simulations usually do not generate basins other than the equilibrium basins. Thus, they provide no information about the free energy $f$ that appears in (19).

It should be clear that depending on the complexity of the basin potential, there are many ways to express $f(T)$ as a function of $\mathcal{E}$. For example, the anharmonicity, to be represented in short by a set of parameters $a$, of the equilibrium basin will also depend on $T$. Now, we may express both $\nu$ and $a$ as a function of $\mathcal{E}$, or decide only to express $\nu$ as a function of $\mathcal{E}$, and leave $a$ as a function of $T$. This will give us two different forms of the equilibrium basin free energy, with both carrying the same information as a function of $T$, but not as a function of $\mathcal{E}$. Thus, such representations are obviously not unique. This is because of the independence of the basin free energy and $\mathcal{E}$. On the other hand, if a quantity has an explicit $\mathcal{E}$-dependence, we can immediately obtain its equilibrium value at a given $T$ by replacing $\mathcal{E}$ by $\mathcal{E}$. For example, $S_{\text{BM}}(\mathcal{E})$ can be expressed in a unique way as a function of $T$ by identifying $S_{\text{BM}}(T) = S_{\text{BM}}(\mathcal{E})$.

The above argument is easily extended to expressing thermodynamic quantities in terms of $\mathcal{E}^{\text{LB}}(T), \mathcal{E}^{\text{MPB}}(T)$, or any other particular average energy related to the basins. There is nothing unique about the BM energy in the landscape, except possibly at low temperatures where the equilibrium free energy is close to $\mathcal{E}(T)$.

In summary, we have made a distinction between basins and equilibrium basins and quantities related to them, which is usually not done. With this distinction in place, we have shown that the shifted basin free energy is independent of particular basin energies like that of BM, LB, MPB, etc. It is a function only of $T$. Thus, the equilibrium basin free energy is also a function of $T$, which is consistent with the first assumption of Goldstein. It is possible to express the equilibrium basin energy as a function of $\mathcal{E}(T), \mathcal{E}^{\text{LB}}(T), \mathcal{E}^{\text{MPB}}(T)$ etc. in presumably many ways, as discussed above, but only if $\mathcal{E}(T), \mathcal{E}^{\text{LB}}(T), \mathcal{E}^{\text{MPB}}(T)$ etc. are monotonic functions of $T$. The unshifted equilibrium BC free energy $\mathcal{F}$ that contributes to is also independent of the BM energy $\mathcal{E}$ by construction. This is consistent with the second assumption of Goldstein, albeit in a modified form. Thus, the configurational states that are to be associated with the entire topology of the basins cannot be characterized simply by their BM energies $\mathcal{E}$, LB energies $\mathcal{E}^{\text{LB}}$, MPB energy $\mathcal{E}^{\text{MPB}}$ or some other particular basin energy; however, the basin free energy can be used to specify the configurational states. The current analysis deals only with the basin free energies. We have found that there is not one average BC of a given average BM energy $\mathcal{E}(T)$, but many different BC’s are explored unless $S(T) = 0$.

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