A stroll in the energy landscape

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We review recent results on the potential energy landscape (PES) of model liquids. The role of saddle-points in the PES in connecting dynamics to statics is investigated, confirming that a change between minima-dominated and saddle-dominated regions of the PES explored in equilibrium happens around the Mode Coupling Temperature. The structure of the low-energy saddles in the basins is found to be simple and hierarchically organized; the presence of saddles nearby in energy to the local minima indicates that, at non-cryogenic temperatures, entropic bottlenecks limit the dynamics.

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The study of the properties of the free energy landscape and/or of the potential energy surface (PES) and their connection with the slow dynamics in undercooled liquids and disordered systems is a topic of current research. The original idea of Goldstein of considering the atomic dynamics of undercooled liquids as the incoherent superposition of a vibrational motion confined in the basin of attraction of local minima of the PES, interspersed by jumps among the basins of different minima, was later developed in a formal theory by Stillinger and Weber. These authors define the basin of attraction of a given local minimum of the PES as the set of all that points in configuration space who are linked to the minimum through a steepest descent path. It is obvious that - according to this definition - the basins of attraction generate a complete partition of the configurational space. Consequently, Stillinger and Weber write the partition function as

$$Z = \sum_{\{B\}} Z_B$$

where \( \{B\} \) indicates the set of all the basins and \( Z_B \) is the partition function restricted to the basin \( B \). The points belonging to the borders \( \partial B \) of the basins are safely excluded from the calculation of the partition function, as they form a set of zero measure.

In this way Stillinger and Weber succeeded to write the free energy of a system with a continuous PES as the sum of the free energy of a typical basin \( F_{\text{basin}}(T, \rho) \) and a term accounting for the multiplicity of basins accessible by the system \( \Omega(T, \rho) = \exp(S_{\text{conf}}(T, \rho)/k_B) \). Excluding the local minima corresponding to crystalline structures, they arrive to an expression for the total free energy of the liquid phase:

$$F_{\text{liquid}} = F_{\text{basin}}(T, \rho) - TS_{\text{conf}}(T, \rho)$$

that can be used to predict, for example, the melting temperature \( T_m \) as that temperature where \( F_{\text{liquid}} \) becomes equal to the free energy of the crystal \( F_{\text{crystal}} \).

According to the Stillinger and Weber idea, the liquid thermodynamics can be derived from the knowledge of the basins of the PES. On the contrary, the proposal of Keyes to use the instantaneous normal mode (INM) theory to predict not only the very short time dynamics but also the long time diffusion processes gives relevance to the process of crossing the borders of the basins and, therefore, to the structure of these borders. In the INM approach, the local curvature of the PES is calculated along equilibrated molecular dynamics (MD) trajectories. The idea is to reconstruct the global shape of the landscape explored from local information. For example, if the system is near enough to a local minimum, the local curvatures of the PES will be all positive and similar in value to the curvatures of the nearby minimum. On the other hand, points near the borders between basins will have negative curvatures along some directions. In fact, the potential energy has a maximum along any direction crossing a border (Fig. 1b). Although the exact functional form is system dependent, the INM approach suggests that the diffusion coefficient \( D \) is a monotonic function of the fraction of unstable modes \( \langle f_u \rangle \) is found as that temperature where \( \langle N_u \rangle \) is the number of negative eigenvalues of the Hessian matrix evaluated along the actual MD trajectory.

A more quantitative relation between the number of negative curvature of the PES and the diffusion coefficient stems from the observation that not all the directions with negative curvatures lead to a change of basins: even in the crystalline state, a non-zero \( \langle f_u \rangle \) is found due to the anharmonicities of the potential. Depending on the different authors and on the different model studied, different methods to discriminate the fraction \( \langle f_{\text{diff}} \rangle \) of truly diffusive directions from the whole set of negative curvatures have been proposed. A non zero value of \( \langle f_{\text{diff}} \rangle \) indicates that the trajectory followed by the system is confined to regions of the configurational space near the borders of the basins.

The study of the diffusion coefficient in undercooled liquids naturally leads to a comparison with the Mode-Coupling Theory (MCT). Indeed, the ideal MCT predicts the existence of a finite dynamical critical temperatures \( T_{\text{MCT}} \) at which \( D = 0 \). The ideal mode-coupling transition can be derived under the restricted assumptions of the gaussianity of the fluctuations. The INM approach reveals that at \( T_{\text{MCT}} \) there is a change in the
temperature behaviour of the quantity $<f_{\text{diff}}>$: it becomes numerically zero (Fig. 1b). Therefore one can conclude that at $T_{\text{MCT}}$ the system ceases to be near the borders of the basins and starts to spend most of the time close to the minima.

On a general ground, one has to understand why the system is not already close to the minima at undercooled temperatures $T_{\text{MCT}} < T < T_m$, or, in other words, why the slowing down of the diffusion processes takes place even if the system spend most of the time close to the basin borders. The analysis of Kurchan and Laloux [9] on the properties of borders in high-dimensional configuration spaces indicates a simple reason for this behaviour. In a $N$-dimensional space, (i.e., the configuration space of a system with $N$ degrees of freedom) a basin $B$ has a volume at least of the order $l^N$, where $l$ is a finite length and is the typical distance among configurations in the same basin. We can imagine then to give a fictious volume to the border $\partial B$ considering “belonging to $\partial B$” all the points in a shell of width $\epsilon$ and volume $\sim \epsilon N^N l^{-1}$ near $\partial B$. The fraction of border points is therefore $\epsilon N/l$ indicating that in the thermodynamic limit $N \rightarrow \infty$ most of the volume of the basins is located in a shell of width $\epsilon \sim 1/N$ near the borders. The numerically observed decrease of $<f_{\text{diff}}>$ with the temperature gives us further indications on the structure of the borders. At high temperatures, the system populates regions of the borders that are in common to many basins, while near $T_{\text{MCT}}$ the system is near regions of the borders in common to few basins; therefore the regions of the borders in common to few basins have a smaller volume compared to regions in commons to many basins. This seems to indicate a hierarchical organization of the configuration space [14]. Indeed, let’s assume that we are able to study the potential energy $U$ restricted to the borders $\partial B$ of the basins. This restricted PES is an $(N-1)$-dimensional manifold where all the stationary points $\{\vec{\Phi}\}$ have their order decreased by one: so, the saddles of order one become the local minima of the restricted $(N-1)$-dimensional PES and partition this manifold in basins. Again, if the system is at high temperatures, the trajectories will be localized near the $(N-2)$-dimensional borders of the $(N-1)$-dimensional basins of attractions; so, one can iterate the procedure until one consider the relevant $(N-i)$-dimensional manifold in the nearby of which equilibrium trajectories are “almost always” within some small distance (with the order $i$ less than or equal to $N < f_{\text{diff}}>$).

Following the previous rationale, in a rough way, one could write the partition function of the system as

$$Z = \sum_i Z_{M_i}$$

where $M_i$ is the set of points in common to $i$ basins and $Z_{M_i}$ is the partition function restricted to the $(N-i)$ dimensional manifold $M_i$. The local minima of the potential energy $U$ restricted to $M_i$ are the saddles of order $i$ in the unrestricted configuration space. Although from the strict point of measure the manifolds $M_i$ have zero measure, we know from the INM studies that at temperatures $T > T_{\text{MCT}}$ the system is in the nearby of some manifold $M_i(T)$ with $\epsilon(T) > 0$. In order to give an operational definition of such partition of the space in basins of attractions of the saddles, one has to give a finite volume to the borders. To this aim, two recent studies [11, 12] have used the pseudo-potential introduced by Stillinger [13]:

$$\Phi = |\nabla U|^2.$$  

It is worth to note that the stationary point of any order of the PES are absolute minima of such potential (in particular they are characterized by $\Phi = 0$), but there exist minima of $\Phi$ - those with $\Phi \neq 0$ - that are not stationary point of $U$. This implies that the use of $\Phi$ is not rigorously correct if the goal is to obtain a partition of the configuration space in basins of attractions of saddles of different orders.

The choice of $\Phi$ provides anyhow a partitioning of the configuration space in basins of attraction of its local minima. As shown recently in [14] and confirmed by a more detailed analysis by us [15], the majority of local minima of $\Phi$ are not true saddles but present a 2% fraction of directions which are indeed inflection points. Despite this, the $T$-dependence of the number and energy location of these “quasi-saddles” carries informations on the dynamical slowing down upon cooling [11]. Therefore, although not all the minima of $\Phi$ found can be classified as “true” saddles [14], we will still assume that they are a good sampling of the PES and therefore that the “true” saddles maintain the same characteristics (i.e. curvatures, number of negative directions, energy) of the found local minima of $\Phi$; in this respect, we will continue using the word “saddles” in this manuscript, keeping in mind that we refer to such minima.

For the case of simple model liquids the order $<N_s>$ and the energy of the saddles explored during the MD simulations have determined [11, 12]. As a result, the saddle’s order has been found to be a decreasing function of the temperature and to become zero at the $T_{\text{MCT}}$ temperature of the system under considerations. This result confirms the role of $T_{\text{MCT}}$ as a crossover temperature from a dynamics near the basins’s borders ($<N_s> > 0$) to a dynamics mainly localized inside the basins ($<N_s> = 0$) [16]. Given this findings, the strong non-Arrhenius increase of the relaxation times of the dynamics approaching $T_{\text{MCT}}$ from above can be explained with the decrease of the diffusive direction, whose number is proportional to $<N_s>$. Indeed, although the system does not need to cross any energy barrier to “jump the ridge” among basin, the exploration of the configuration space is slower as the connectivity (i.e. the number of adjacent basins that the system can freely reach) among basins decreases.

A direct evidence of situations in which, although the energy of the saddles is significantly less then the energy of the system, the system is trapped in the basin of attraction of a local minimum, is found in [17], where the
connectivity between the crystalline ground state and the adjacent local minima is analyzed for a model of the crystalline compound \( MgF_2 \). Moreover, it is found in Ref. [17] that, at higher energies, saddles connecting several minima make up a sizable fraction of the transition region.

A further confirmation of the "entropic" - rather than "energetic" - origin of the slowing down of the dynamics is given by numerical aging experiments. For Lennard-Jones liquids, it has been shown that in the aging following a deep quench, the system follows quasi-equilibrium states [18] during which short time dynamics is intra-basin vibration, while long time dynamics is dominated by the slow search of deeper and deeper local minima. The work of Angelani et al. [19] shows that, after a short transient, the system changes basins crossing saddles of order one without any energy activated process.

The result that at \( T_{MCT} \) the value of \( \langle N_s \rangle \) approaches zero has lead to the interpretation of the mode coupling critical temperature as the threshold below which the diffusive dynamics becomes activated with potential energy barriers that the system needs to overcome in order to cross the border between basins [20]. We show here - after a careful definition of the meaning of the term "activated processes" in the framework of the PES description of the dynamics - that it is at least unnecessary to invoke potential energy barrier crossing, and that there is no qualitative change in the way the system change basins below or above \( T_{MCT} \). What is qualitatively different on crossing \( T_{MCT} \) is the vanishing probability of occupying a basin of a saddle below \( T_{MCT} \).

Let’s first discuss the concept of activated processes in the framework of landscape theory. Landscape theory considers the motion of a representative point in an \( N \)-dimensional configuration space; in the thermodynamic limit \( N \to \infty \), the value of thermodynamic quantities like the average potential energy \( U \) becomes determined apart of fluctuations of order \( 1/\sqrt{N} \) [21]. Although in ergodic theory the complexity of the landscape is not explicitly considered but as the hypothesized source of random couplings enforcing the large-numbers law and the ergodicity [22], the apparatus of the ergodic theory approach to the foundation of statistical mechanics is based on the analysis of the motion of the system on isopotential manifolds of the PES. The exploration of such manifolds is purely entropic, and no fluctuation in energy is considered. Obviously, for \( N \) large enough, one can always consider a subset of the system with a finite number \( M \) degrees of freedom. This subset can be then considered as a canonical system of \( M \) degrees of freedom with finite fluctuations of order \( 1/\sqrt{M} \) [21]. In general, it is possible to select a subset of coordinates \( \{\omega\} \), the "reaction" coordinates) relevant to the process under consideration, as for example the coordinate describing the motion across the basin’s border. In this case the potential energy of the subset along the reaction coordinate goes through a maximum (a saddle point in the configurational space). The other degrees of freedom can be considered as a "thermal bath" for the reaction coordinate.

Our aim is now to show that both approaches - the one considering the systems as a whole moving on a constant potential surface and the one that focus the attention on the reaction coordinate and consider the rest of the system as a thermal bath - can be used to correctly determine the "transition rates", i. e. that quantity that control the inter-basins dynamics.

According to the second point of view, the expression of the free energy \( F(\omega, k_BT, \ldots) \) is found integrating over the degrees of freedom orthogonal to \( \omega \), and the result is the usual free energy in the canonical ensemble. This free energy defines the pure states as local minima of the free energy (a pure state is now a not necessarily compact set of points in the configuration space); the free energy barriers among these pure states signal transitions among states. Yet, once a coarse-grained description of the system in terms of reaction coordinates \( \omega \) is given, the possibility of discriminating among energy and entropy barriers is found. As a back-of-the-envelope calculation to illustrate the concept, let’s consider a collection of \( N \) harmonic degrees of freedom plus a double well degree of freedom with two equal minima separated by an energy barrier of height \( \Delta \). The reaction coordinate corresponds obviously to the anharmonic degree, and the transition rate among the minima can be calculated to be \( \propto \exp(−\Delta/k_BT) \). If, on the contrary, we work in the spirit of the second point of view, i. e. with trajectories at constant potential energy \( U \), we can estimate the transition rate as a ratio of volumes, and specifically as the ratio of the volume \( \sim (\sqrt{U})^N \) relative to the time that the system spend in the basin of a minimum and the volume \( \sim (\sqrt{U−\Delta})^N \) pertaining to the time spent in the order-one saddle basin. In the thermodynamic limit, where \( N \to \infty \) and \( U \to Nk_BT/2 \), we have that the transition probability \( (1−2\Delta/Nk_BT)^{N/2} \) converges to \( \exp(−\Delta/k_BT) \). We can conclude that the two points of view give rise to the same expression for the transition probability.

As a further example we present the numerical comparison between the "true" dynamics of a finite size systems and a fictious dynamics where the same system is forced to evolve at constant potential energy. In particular, we study the self diffusion coefficient in the so called "Trigonometric Model" (TM), introduced by Madan and Keyes [23] as a dynamical system with a very simple structure of the PES. In the TM each degree of freedom is independent from the other and experiences a periodic external force, in particular the TM potential energy has the form:

\[
V(\{\omega\}_{i=1..N}) = \sum_{i=1}^{N} \Delta[1−\cos(\pi x_i/d_0)].
\]

Despite its simplicity, the PES of this model contains some features that have been retrieved in more realistic glasses. The TM shares with the binary mixture - and with the modified - LJ system investigated in Ref. [11] the
existence of a regular organization of the saddles above a given minimum (the elevation in energy of the saddle is proportional to the saddle’s order) and a regular distribution of the minima in the configurational space (nearest neighbor minima lie at a well defined Euclidean distance). What the TM misses is the existence of minima with different energies, a characteristic of realistic glasses [24]. This deficiency is not important here, as we want only to select a toy model to compare the "canonical" and "iso-potential" dynamics. In order to simplify the calculation, in this example we treat the dynamical evolution of the system following a Langevin dynamics, but with a constrain that obliges the system to move at constant potential energy. The motion at constant potential energy implies that \( \sum_i \dot{x}_i \nabla_i V = 0 \), and this condition is automatically satisfied by modifying the equation of motion (10) as:

\[
\dot{x}_i(t) = \eta_i - \frac{\sum_j (\eta_j \nabla_j V)}{\sum_j (\nabla_j V)^2} \nabla_i V
\]

The evolution of \( N=1000 \) variables obeying Eq. (10) has been solved numerically at different temperatures. The diffusion coefficients calculated in these runs (for each \( T \)) were made 500 replica each one 500 000 time steps long and are reported in Fig. 4 (open dots). The comparison between the values of \( D \) evaluated along canonical trajectories (full lines) and along iso-potential trajectories (open circles) clearly indicates that, already for not-too-large system sizes (\( N=1000 \)), the "true" dynamics take place along constant potential energy manifolds, and that the potential energy fluctuations, that are present in the canonical calculation, are not relevant for describing the diffusion process.

As we have shown, and substantiated with the previous examples, in the thermodynamic limit the dynamics of the system as a whole takes place along constant potential energy manifolds, the fluctuation becoming irrelevant. In this framework, i.e. discussing the under-cooled dynamics as motion of the representative point in the configuration space, the notion of activated process becomes irrelevant as well. Either at high and low temperature, above or below \( T_{MCT} \), the representative point in the configuration space never crosses potential energy barriers. The slowing down of the dynamics with decreasing \( T \) is a consequence of a topological properties of the PES, i.e. the decreasing number of the accessible iso-potential paths between minima with decreasing potential energy. Some of these open paths still exist even on the typical constant potential energy manifolds visited at temperature well below \( T_{MCT} \), as shown, for example, in Ref. [11]. One can conclude that the dynamical slowing down is fully entropy controlled and no qualitative differences in the way the system changes basins are observed crossing \( T_{MCT} \). On the contrary, a qualitative change in the dynamics is expected to take place at even lower \( T \) (at the Kautzmann temperature \( T_K \)), where the number of accessible basins becomes non extensive. In this respect, whether or not \( T_K \) is different from zero is still matter of debate.

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\[
D = \frac{\Gamma}{\beta Z(\beta)} \frac{1}{Z(-\beta)}
\]

where \( Z(\beta) \) is the partition function for a single degree of freedom. For potentials - like that of Eq. (6) - having a skew symmetry, \( V(x) = 2\Delta - V(x - d_x/2) \), equation (7) simplifies to:

\[
D = \frac{\Gamma e^{-2\beta \Delta}}{\beta Z^2(\beta)}.
\]

Finally, by calculating the partition function for the TM, one gets

\[
D = \frac{\Gamma}{\beta} \frac{1}{Z(\beta)}
\]

where \( L_n(x) \) is the Bessel function of order 0. The dimensionless quantity \( D/D_{\text{free}} \), where \( D_{\text{free}} = \Gamma k_B T \) is the diffusion coefficient for free brownian motion, is reported as a function of \( \theta = k_B T/\Delta \) in Fig. 4 (full line).

As second step, we calculate the diffusion coefficient for the same potential model and the same stochastic dynamics, but with a constrain that obliges the system to move at constant potential energy. The motion at constant potential energy implies that \( \sum_i \dot{x}_i \nabla_i V = 0 \), and this condition is automatically satisfied by modifying the equation of motion (10) as:

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**FIG. 1.** a) Sketch of the potential energy surface (PES) along a direction with negative curvature that could lead to inter-basin diffusion. The marked point represents the position of the system; for \( T > T_{MCT} \) the apparent energy barrier between this point and the top of the PES along the direction considered is less than \( \sim 10^{-2} k_B T \) for the models studied. Although the section of the PES in this example has two minima along the direction of the eigenmode associated with this negatively curved direction, it can be that these apparent minima lead to the same basin b) The fraction < \( f_{\text{diff}} \) > of diffusive modes in the SPC/E model for water goes to zero at the mode-coupling transition temperature \( T_{MCT} \) (from ref. [20]).
FIG. 2. Effect on the landscape from switching from the potential $U$ to the pseudo-potential $|\nabla U|^2$: the saddle $S$ becomes a minimum with a finite basin of attraction, the basins of attraction of the minima $A$ and $B$ become smaller. Note that the picture is a two-dimensional sketch, so that the border of the basins “acquires” a small volume: in higher dimensions the effect is enhanced.

FIG. 3. a) Temperature dependence of the potential energy of the system, of the saddles and of the minima for the Modified Lennard-Jones system of ref. [11]. The full squares indicate extrapolations of the energies at $T = T_{MCT}$. Note that, in the range of the graph, $U(T_{MCT})$ is still much above the potential energy range of the saddles. b) Schematic representation of the motion of the system at a temperature slightly below $T_{MCT}$. For a big system, the motion happens essentially along constant potential energy. Although there are still saddles below the trajectory, the system is seldom near the border above the saddles; when the trajectory meets the border, a change of basin happens without energy activation.
FIG. 4. Diffusion in the trigonometric model [23]. The continuous line is the analytical solution for the dynamics in the canonical ensemble [25]; circles are numerical calculations for the constant potential energy dynamics (Eq. 10).