Landscape Approach to Glass Transition and Relaxation

- Four lectures on “The Landscape Approach”.
  (March 23, 25, 30, April 1).

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- Reading Resources:
  Varshneya’s Book (Ch # 13, section 13.5.3)
  FH Stillinger, Science, 267 (1995) 1935.
  F. Sciortino, J. Stat. Mech. (Theory and Exp.) P05015 (2005).
  PK Gupta & JC Mauro, J. Chem. Phys, 126 (2007) 224504.
  JC Mauro et al, Scientific Modeling and Simulation, 15 (2008) 241.

Approximate outline of lectures:

1: Basic Concepts (Geometry and topology)

2: Basic Concepts (Dynamics and barriers)

3: The liquid to glass transition

4. Relaxation in glasses

What is the “Landscape Approach”?

- The object of the landscape approach is a macroscopic system containing a large number (N ~ 10^{23}) of interacting atoms (or ions, or molecules).
- Macroscopic systems are typically observed at a macroscopic level ($\geq$ 1 micron). The goal of Materials Science is to provide a detailed understanding of the observable chemical and physical properties of macroscopic material systems and to answer questions such as: “how and why” are different properties related to each other, “how and why” do properties change with time and temperature, and “how and why” different systems behave differently.
- The “how” part can be answered using experimental results and macroscopic theories such as thermodynamics, kinetics, elasticity, etc.
- The “why” part is difficult and requires study of systems at a microscopic (atomistic) level. The connection between microscopic and macroscopic properties is provided by statistical physics.
- The landscape approach is a statistical physics based theoretical framework that is especially suitable to condensed systems such as liquids and glasses.

Macroscopic state (Y) of a system

A macroscopic state (or macro-state) describes a system in terms of a *small* number of observable (measurable) properties called state variables.
Examples of macro-states are:

- Equilibrium (stable or thermodynamic) state: Ex: a liquid above $T_{melt}(P)$.

It is described by state variables (T, V, N) or (T, P,N) where T = temperature, P = pressure, V = volume, N = total number of atoms]. These state variables are called external parameters as they are controlled from the outside by an experimentalist.

- Meta-stable states: Ex: a super-cooled liquid.

These are essentially equilibrium states with some internal configurational constraints (χ). These states ($T, V, N \mid \chi$) behave as equilibrium states so long as the constraints are not violated.

- Non-equilibrium states: Ex: the glassy state.

Non-equilibrium states are unstable and time dependent. Some non-equilibrium states can be described by including a set of internal dynamic constraints, z(t). These constraints are also called internal parameters (or “order parameters” in the glass literature).

Microscopic (or structural) configuration (X)

- A microscopic configuration *(or micro-state)* specifies the position vectors (r_i) of all N atoms and the external constraints.

Ex: When the volume (V) of the system and the total number of atoms (N) in a system are specified, a micro-state (X) is given by the 3N position variables $\{r_1, r_2, \ldots\ldots, r_N\}$. Note that X contains very detailed information since N is very large ~ 10^{23}).

- Important: Since a macrostate has only a few variables, *it follows that a large number of microscopic states correspond to one and the same macroscopic state (Y).*

Configuration space (Ω)

- The configuration space is the ensemble of all possible (microscopic) configurations of a system for a specified set of external parameters (N,V).

- Ω is a continuous, 3N dimensional space with the constraint that each atom coordinate lies inside the volume V.

- For a givem macrostate Y, it is not possible to know the exact microscopic state of a system. One can specify only a probability, P(X, t |Y), that the system is in a particular microstate, X, at some time t for a given macro-state Y.

- Statistical physics tells us how P(X, t | Y) changes with time for non-equilibrium systems when Y is fixed.

Atomic interactions

- Atoms are constantly exerting forces on each other (except in hypothetical materials like ideal gas). Atomic interactions carry the “genetic” information about a system. They determine all equilibrium and non-equilibrium properties of a system. Precise details of interactions are obtained only from quantum mechanical (ab-initio) calculations. In landscape approach, it is assumed that all atomic interactions are known.

- An atomic interaction is described by the potential energy (u) of interaction as a function of coordinates of the centers of participating atoms. Interaction force on an atom i is equal to the gradient of the interaction energy with respect to the position of the i-th atom, - (∇_i u).

- Most significant interactions are pairwise (or simply pair) interactions, u(r_i, r_j), depending *only* on the locations of the two atoms i and j (and independent of positions of all other atoms). A vast majority of pair potentials, depend only on the scalar distance (r) between the two participating atoms:

$$u = u(r)$$

$$r = | r_i - r_j |$$

Atomic interactions (contd.)

- The “zero” of the interaction energy corresponds to the configuration where distances between participating atoms are infinite.

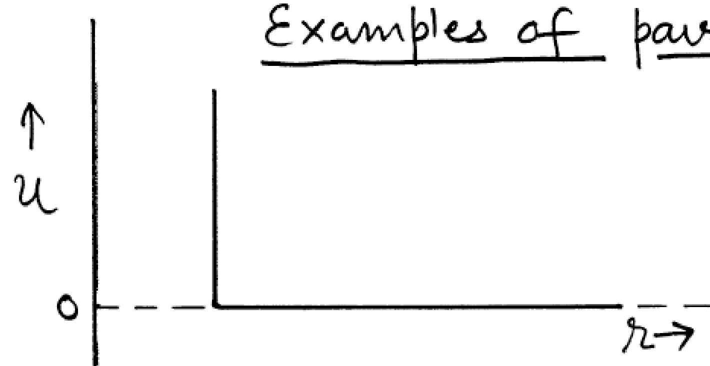
- When atoms are close together, the interaction energy is positive and the interaction is called repulsive. At larger distances, the interaction energy is negative and the interaction is called attractive.

- All interactions are bounded from below: $u(r) \geq - u_o$.

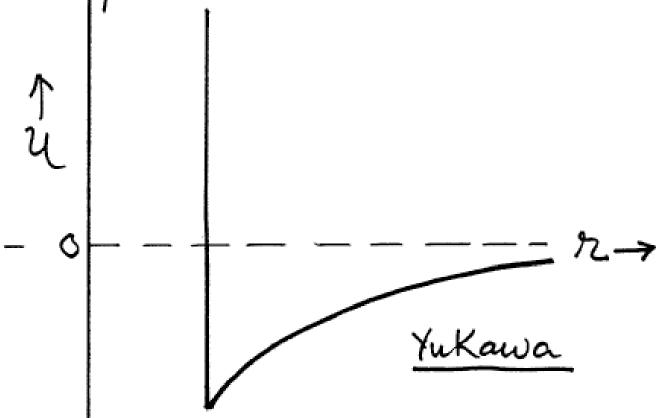
- The participating atom centers i and j cannot occupy the same position at the same time, since u becomes infinite. Such configurations are physically not possible and are excluded from consideration.

- Some simple examples of pair interactions u(r) are shown on the next page:

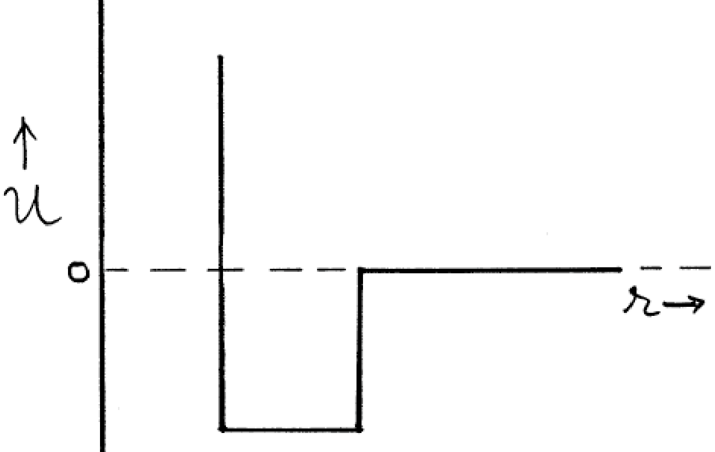
Examples of pair-potentials



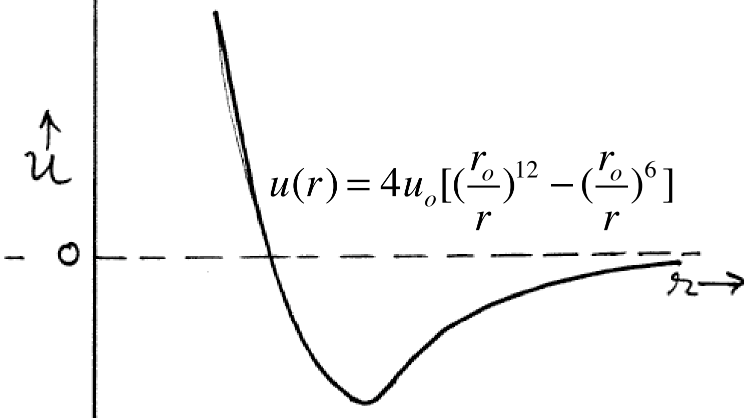
Hard Core



Yukawa



Square-well



$$u(r) = 4u_o[(\frac{r_o}{r})^{12} - (\frac{r_o}{r})^{6}]$$

Lennard-Jones (LJ)

Potential Energy ,Φ(X), of a configuration

$$\Phi(X) = \sum_{pairs} u_{ij}(X) + many.body.potentials$$

- The variation of Φ as a function of X over the entire Ω describes a potential energy surface in a (3N + 1) dimensional space (one dimension corresponding to energy and 3N to X). This potential energy surface is called the potential energy landscape, PEL (or the energy landscape or simply the landscape).

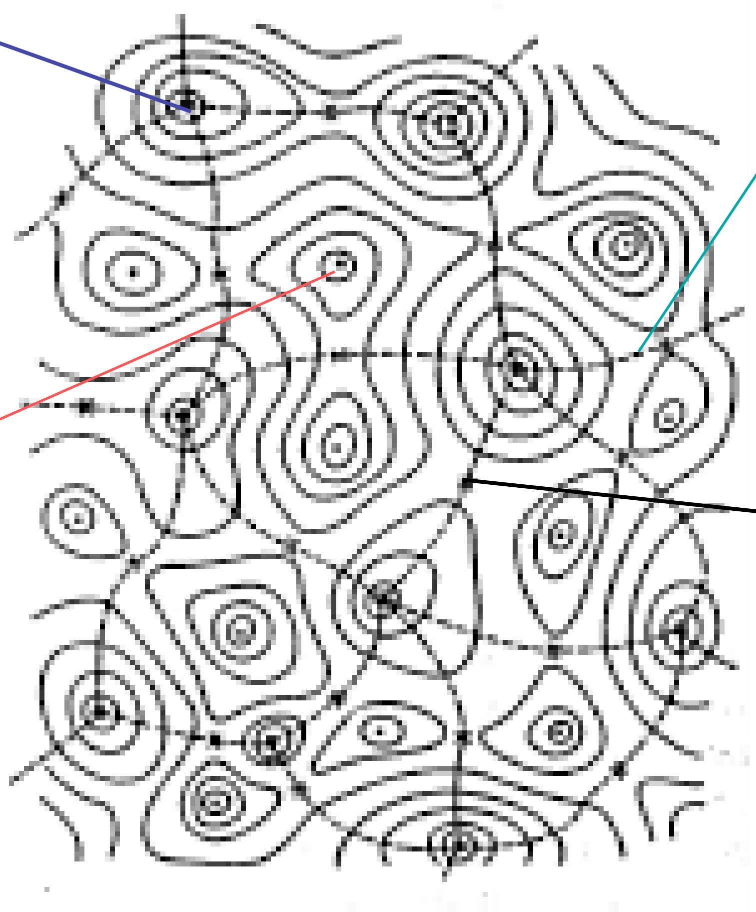
Some properties of PEL:

- Lower bound: $\Phi(X) \geq -N\phi_{\min}$

- PEL is continuous and differentiable.

- PEL is a hyper-rugged surface containing a large number of maxima (mountain tops), minima (valley bottoms), and saddles (mountain passes).

- PEL of a system is independent of temperature.



Mountain top

Ridge

Valley bottom
(Local minimum)

Mountain Pass
(Transition State)

Potential energy contour diagram

[FH Stillinger and TA Weber, Science, 225 (1084) 983].

Important features of a landscape

1. Geometrical:
    - Global minimum
    - Local minima
    - depth (ϕ) distribution of minima
    - Basins

    - Saddle states

2. Topology:
    - Connectivity of neighboring minima
    - Transition paths and barrier heights

Geometrical features of the landscape

1. Saddle states

- Extremum states having no forces are called saddle states:

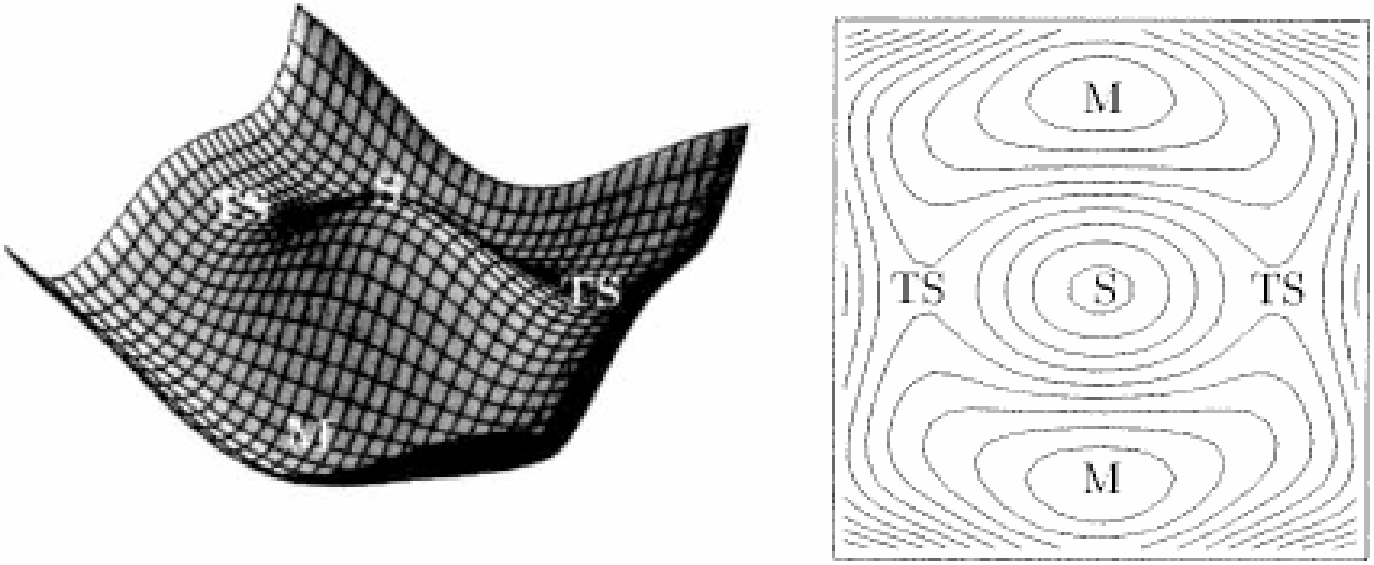
$$\nabla\Phi(saddle) = 0$$

- Each saddle configuration is characterized by 3N eigen-values of the 3N x 3N second derivative curvature matrix (called Hessian), $\nabla^2\Phi\,|_{saddle}$. The eigen-values are the values of the principal curvatures of the PEL at a saddle point.

- The order of a saddle point is defined by the number of its negative eigenvalues.

- Zero-order saddles = all curvatures are positive = local minima
- first order saddles = curvature is negative along one principal direction. These are commonly known as transition states (or activation states).

Contour map and saddle points



(M = minima, TS = transition state, S = second order saddle)

DJ Wales, “Energy Landscapes”, Cambridge (2003).

Geometrical features of the Landscape (contd.)

2. Inherent structures (IS):

- The local minima are called “inherent structures”.
- All local minima are mechanically stable (i.e., all small fluctuations in configuration increase the potential energy of the system).
- ISs are important states as the system prefers to occupy these states.

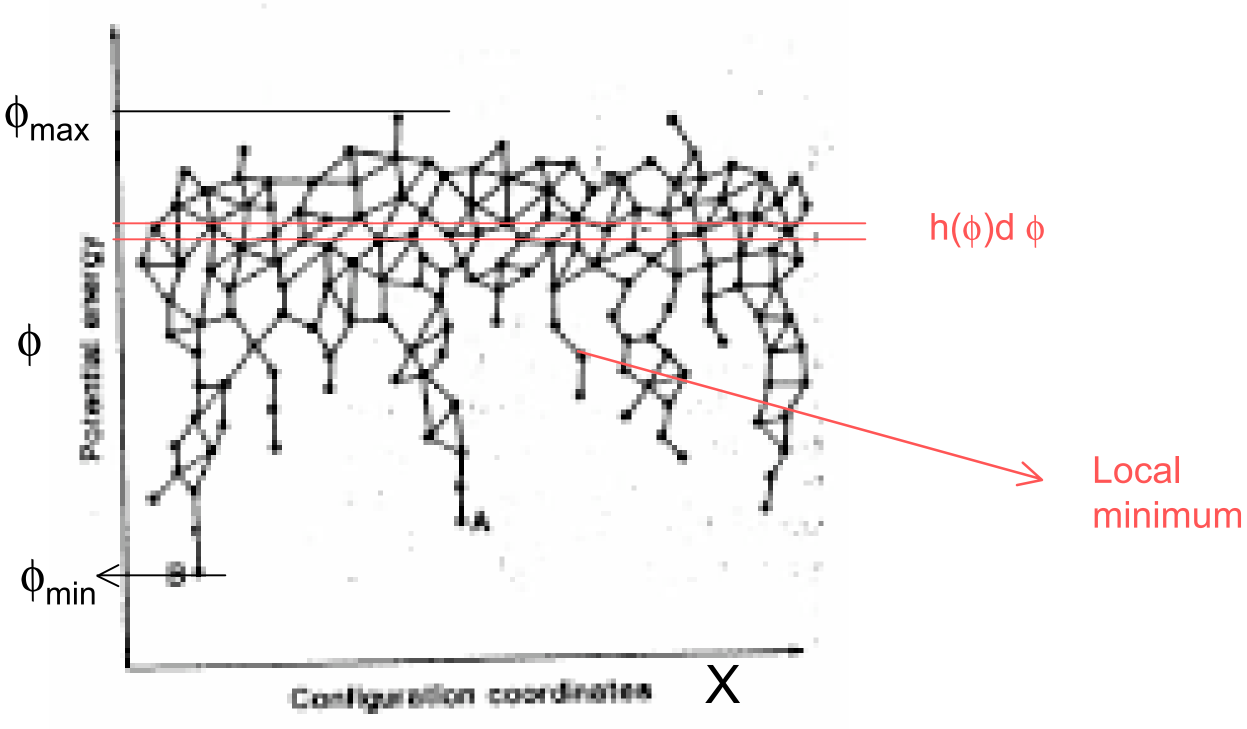
- Let us define the potential energy per atom by $\phi(X) \equiv [\Phi(X) / N]$.

- The inherent structures can be ranked according to their ϕ-values. The number of ISs, $h(\phi)\, d\phi$, having potential energies between ϕ and $\phi+d\phi$ is given by

$$h(\phi, N) = N!\exp[N\sigma(\phi)]$$

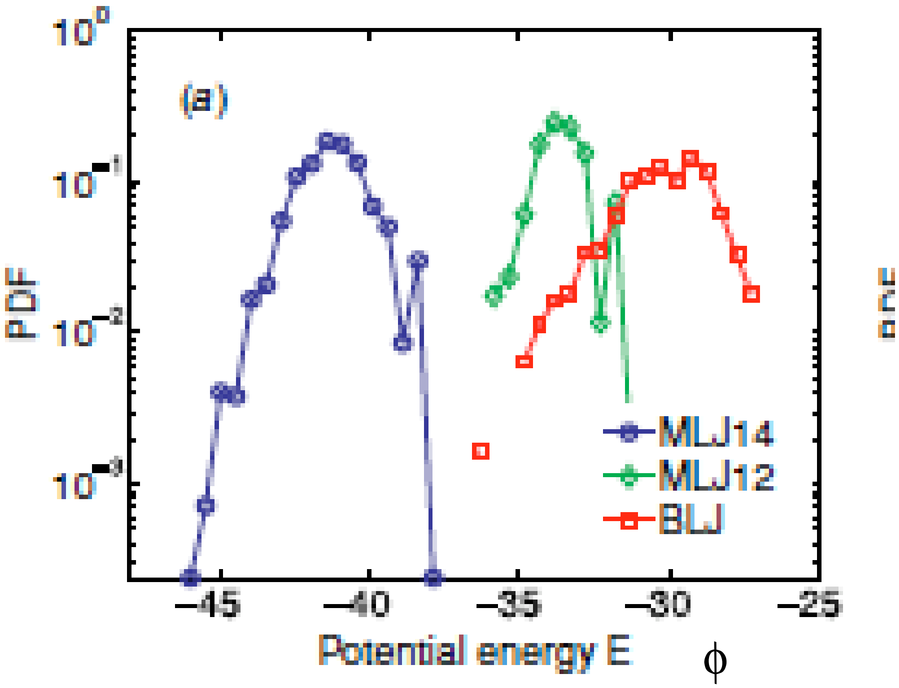
Here $\sigma(\phi)$ is non-negative function of ϕ. The density of ISs ,$h(\phi)$, is zero except when:

$$\phi_{\min}^{IS} < \phi < \phi_{\max}^{IS}$$



[FH Stillinger and TA Weber, Science, 225 (1084) 983].

Lennard-Jones PELs



h(ϕ)

ϕ

[S. carmi et al, J. Phys. A 42 (2009) 105101]

Geometrical features of the landscape (contd.)

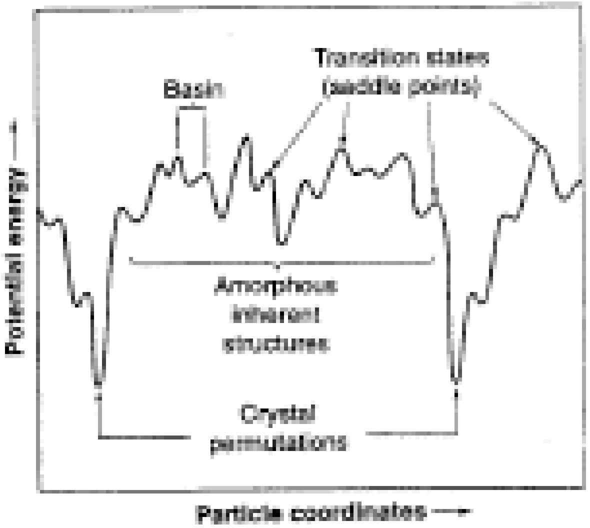
3. Basins:

For each inherent structure (IS), there exists a set of surrounding configurations which lead to that IS after local energy minimization. This set of surrounding configurations is referred to as the basin of attraction (or simply the basin) of that particular IS. Thus, the entire configuration space Ω can be divided into non-overlapping set of basins.

4. Ridges and transition states:

Neighboring basins are separated along ridges that contain the transition states. A simple schematic of a PEL is shown on the next page:

A 2-dim sketch of PEL



[FH Stillinger, Science, 267 (1995) 1935]

Topological features of a landscape

Landscape as a network (nodes and links).

- Each IS is a node of the network.
- Each transition state connects two Iss and forms a network link between two nodes.

Topological measure:

- Degree (k) of connectivity of a node is the number of nodes directly linked to the node under consideration.

Lannard-Jones PEL as a network

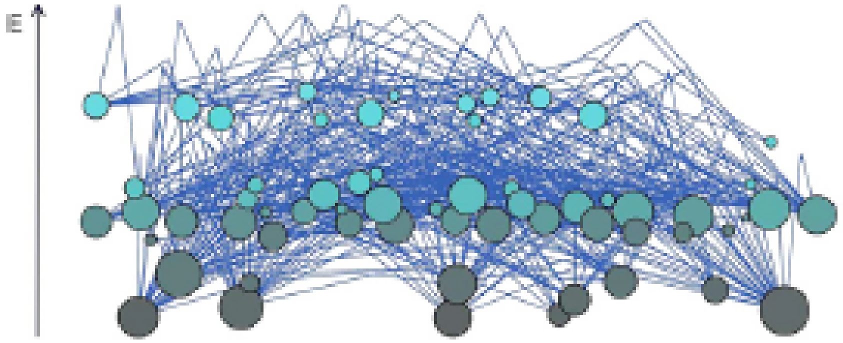
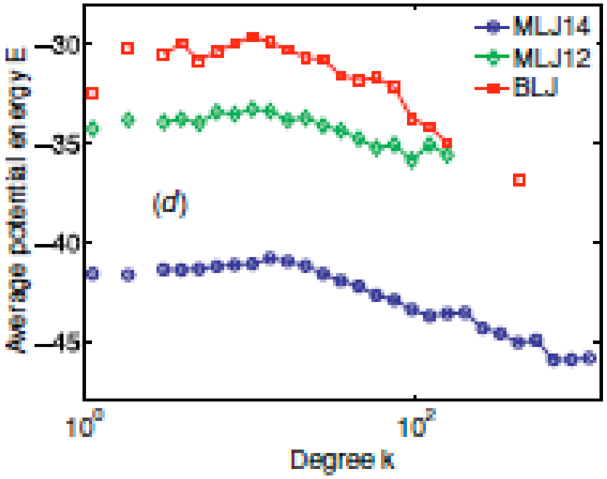


Figure 2. MLJ$_{10}$ network schematic. The vertical axis represents the energy, such that nodes with deeper energy are lower (and darker) in the schematic. Links' cusps correspond to the energies of the saddles, and nodes' sizes are proportional to their degree. It can be seen that highly connected nodes usually correspond to deeper basins.

[S. Carmi et al, J. Phys. A, 42 (2009) 105101]



[S. Carmi et al, J. Phys. A, 42 (2009) 105101]

- Deepest basins are network hubs.

The Potential "Enthalpy" Landscape, $\Psi(X)$.

- For systems, where the macroscopic state is prescribed by a fixed pressure, the volume becomes an additional variable in describing a microscopic state. In this situation, the total energy of the system is called potential enthalpy, $\Psi(X,P)$,and is given by:

$$\Psi(X,P) = \Phi(X) + PV$$

The landscape corresponding to $\Psi(X,P)$ is called the potential enthalpy landscape.

- All features and concepts (such as inherent configurations, basins, transition states, etc.) defined for potential energy landscapes apply equally well to potential enthalpy landscapes.

Landscape of a super-cooled liquid (SCL):

- The lowest energy ISs are associated with the perfect most stable crystalline state.The next lowest ISs belong to defective stable crystals. The next ones may belong to metastable crystalline states. All of these are referred to as crystalline ISs.

- Higher energy ISs tend to be amorphous or liquid like.

- We define PEL(crystal) as the union of all basins each containing at least one crystal (stable or meta-stable) of size equal to or larger than the critical nucleus size.

- The PEL of the super-cooled liquid is defined as follows:

$$\text{PEL (SCL)} \equiv \text{Entire PEL} - \text{PEL(crystal)}.$$

All ISs in a SCL landscape are amorphous. From now on, we consider only PEL(SCL).

The internal energy, U, of a system:

- The internal energy of a system is the sum of its potential energy and the total kinetic energy of all N atoms:

$$U = \Phi(X) + \frac{1}{2}\sum_i m\upsilon_i^2$$

In condensed phases, the kinetic thermal energy is contained in vibrations.

- Since, from equipartition theorem,

$$\frac{1}{2}\sum_i m\upsilon_i^2 = \frac{3}{2} N k_B T$$

It follows that U(X,V,T) = Φ(X) + (3/2) Nk_BT .

Similarly, the enthalpy H(X,P,T)= Φ(X) + PV+ (3/2) Nk_BT.

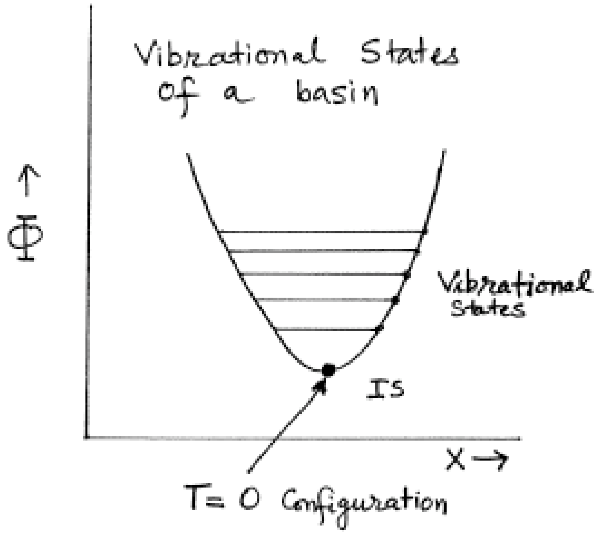
This implies that at low enough temperatures, the properties of a system are dominated by its landscape. It turns out that glass forming super-cooled liquids near the glass transition are in the landscape-dominated regime.

Vibrational states of a landscape:

- All configurations in a basin - with the exception of the inherent configuration - correspond to finite temperature vibrational states.

- Structurally, the vibrational states are temperature-induced distortions of the underlying inherent configuration.

- The properties of the vibrational states can be calculated from the knowledge of the basin shape (that determines the vibrational frequency, ν) and the basin depth.



Configurational states of a landscape:

- The inherent structure is the only non-vibrational configuration (the configuration at absolute zero) in a basin.

- The contributions to the properties of a system from ISs are conventionally referred to as the “configurational” properties.

IS contributions = Configurational contributions

Summary

- Important features of a landscape are geometric and topological.
- Important geometric features are
  - a) inherent structures
  - b) basins
  - c) transition states
- Important topological features are degree of connectivity of inherent structures.
- A macroscopic property of a system

  = Vibrational contribution to the property

  \+ Configurational contribution to the property

  The configurational property originates from contributions from ISs.

- A key advantage of the landscape approach lies in the separation of the vibrational and inherent contributions.

- Degree of connectivity increases with the depth of IS. Deep lying ISs act as hubs in the landscape network.