

# 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 ( $N \sim 10^{23}$ ) 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**) is described by the entire set of observable (measurable) properties of a system. It has been found that these properties are determined by a small number of **state variables** (called external parameters or constraints) which are controlled from outside.

- **Equilibrium (stable or thermodynamic) state**: Ex: a liquid above  $T_{\text{melt}}(P)$ . Typical state variables are:  $(T, V, N)$  or  $(T, P, N)$  where  $T$  = temperature,  $P$  = pressure,  $V$  = volume,  $N$  = total number of atoms].

- **Meta-stable states**: Ex: a super-cooled liquid. These are essentially equilibrium states with some **internal configurational constraints** ( $\chi$ ). State variables are:  $(T, V, N | \chi)$  or  $(T, P, N | \chi)$ .

- **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). State variables are:  $(T, V, N, z(t))$ .

## 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 N position vectors  $\{r_1, r_2, \dots, r_N\}$ . Note that X contains very detailed information since N is very large  $\sim 10^{23}$ ).

- **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)*. Thus, for a given Y, X is not known precisely.

## Configuration space ( $\Omega$ )

- The **configuration space** is the **set** of all possible (microscopic) configurations of a system for a specified set of external parameters (T,N,V).
- $\Omega$  is a **continuous,  $3N$  dimensional space with the constraint that each atom coordinate lies inside the volume  $V$** . Each point of  $\Omega$  is a possible microstate.
- For a given 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 instant of 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 the 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,  $-(\nabla_i u)$ .
- 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:

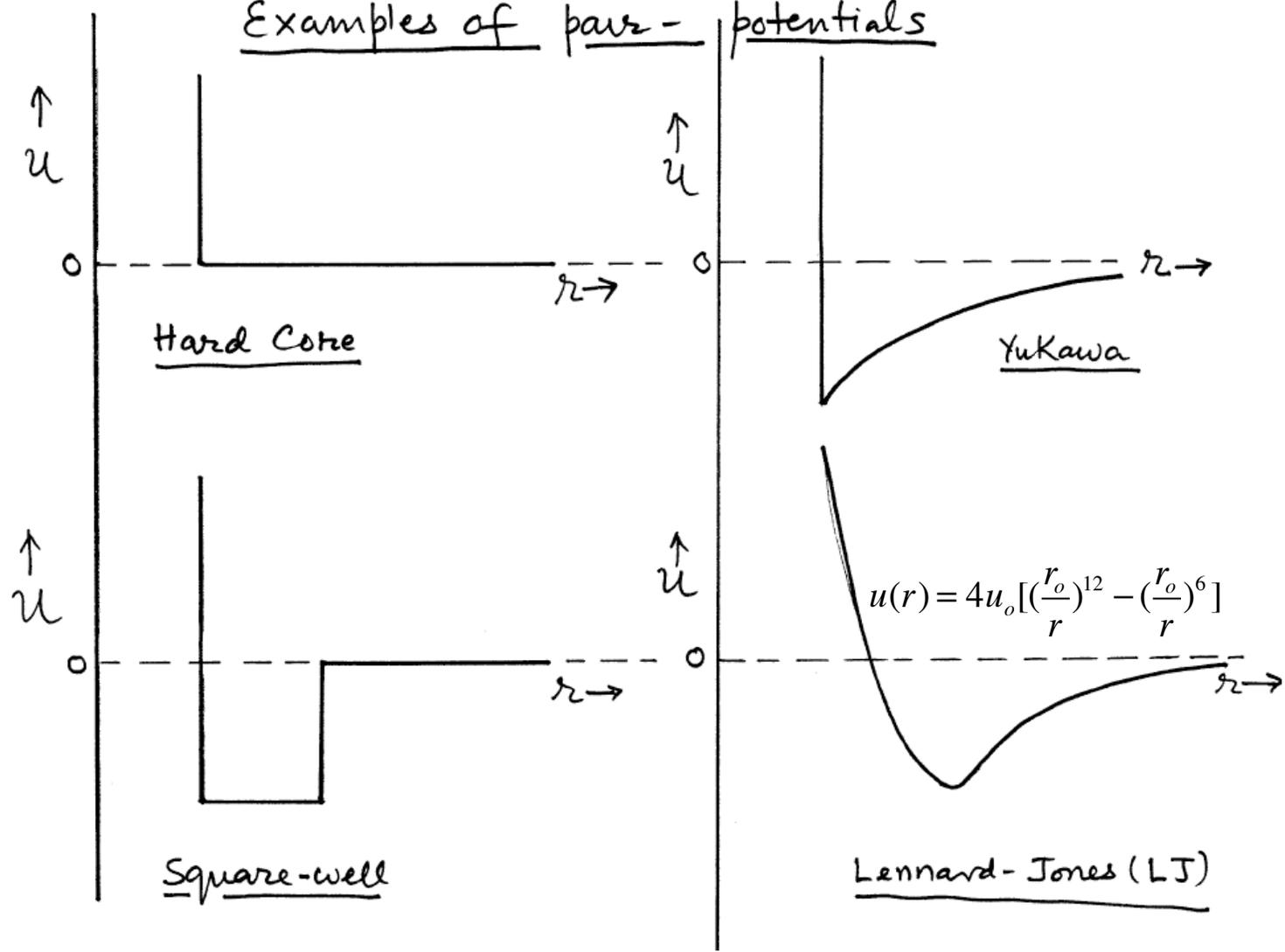
$$u = u(r)$$

$$r = |r_i - r_j|$$

## 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:  $u(r) \geq -u_0$ .
- 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



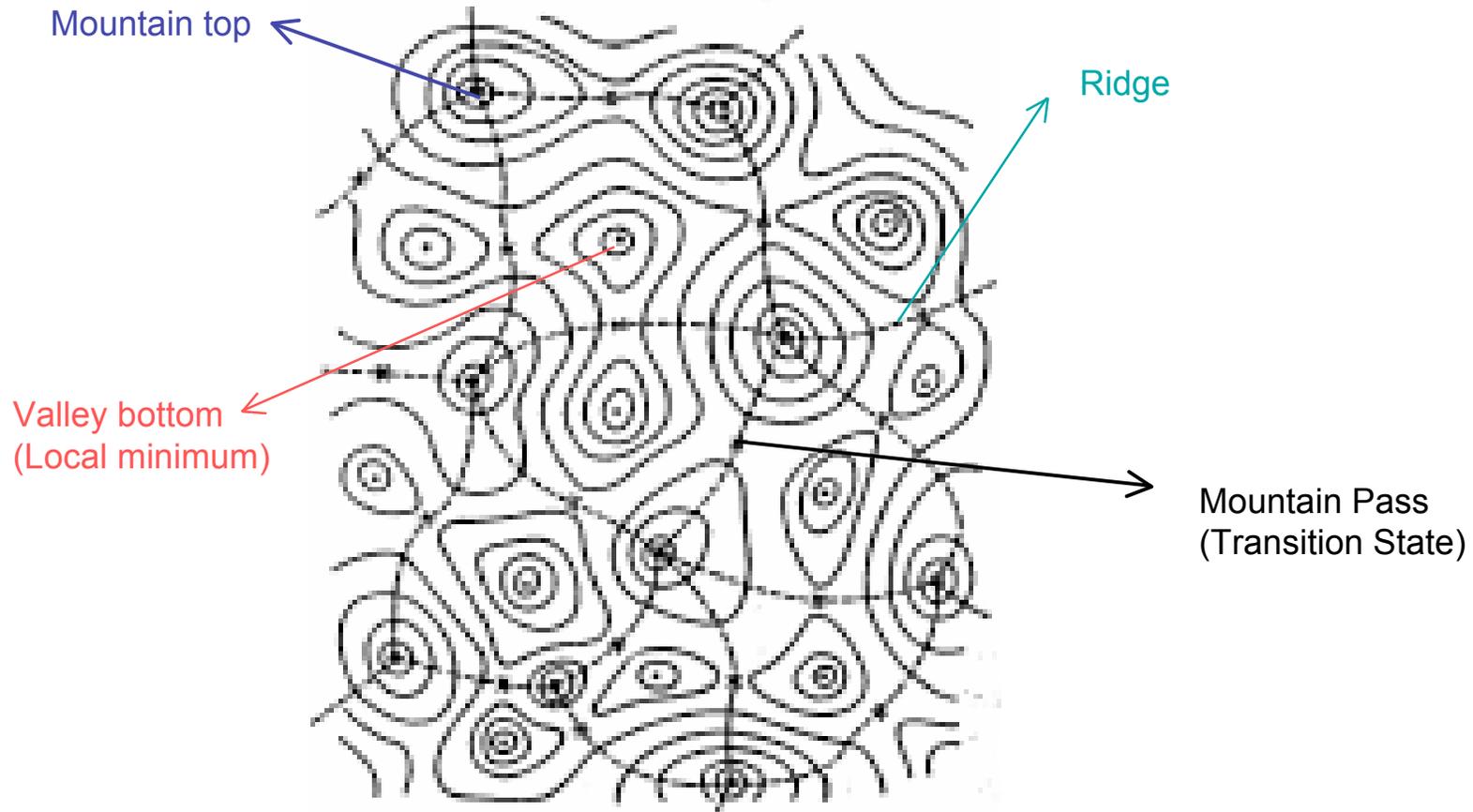
## Potential Energy , $\Phi(X)$ , of a configuration

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

- The variation of  $\Phi$  as a function of  $X$  over the entire  $\Omega$  describes a 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 **multi-dimensional 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.



Potential energy contour diagram

[FH Stillinger and TA Weber, Science, 225 (1084) 1983].

# Important features of a landscape

## 1. Geometrical:

- Global minimum
- Local minima
- depth ( $\phi$ ) distribution of minima
- Basins
  
- Transition states

## 2. Topology:

- Connectivity of neighboring minima
- Transition paths and barrier heights

# Geometrical features of the landscape

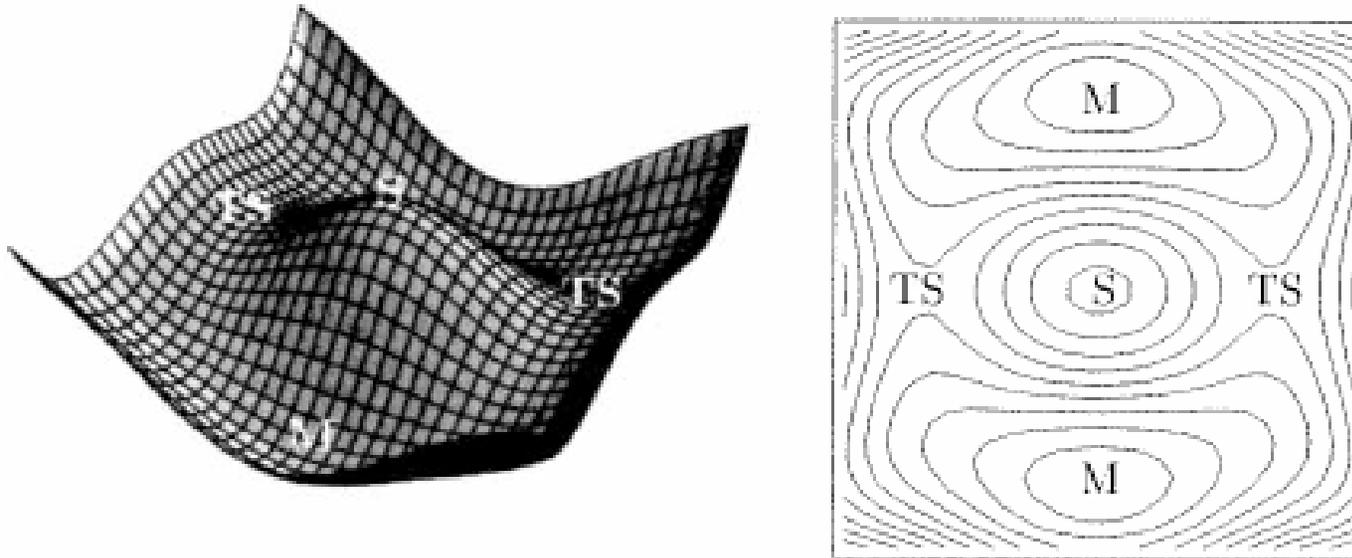
## 1. Saddle states

- 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 (negative principal curvatures).
- 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.)

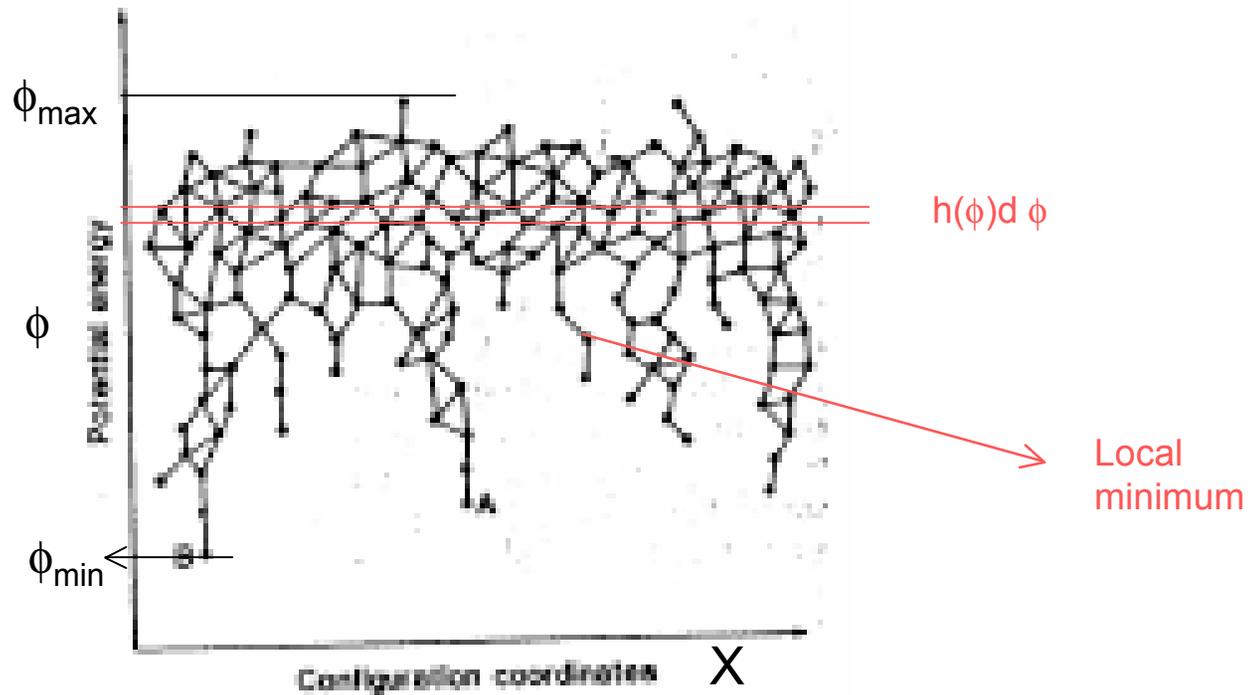
### 2. Inherent structures ( IS):

- 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  $\phi$ -values. The number of ISs,  $h(\phi) d\phi$ , having potential energies between  $\phi$  and  $\phi+d\phi$  is given by

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

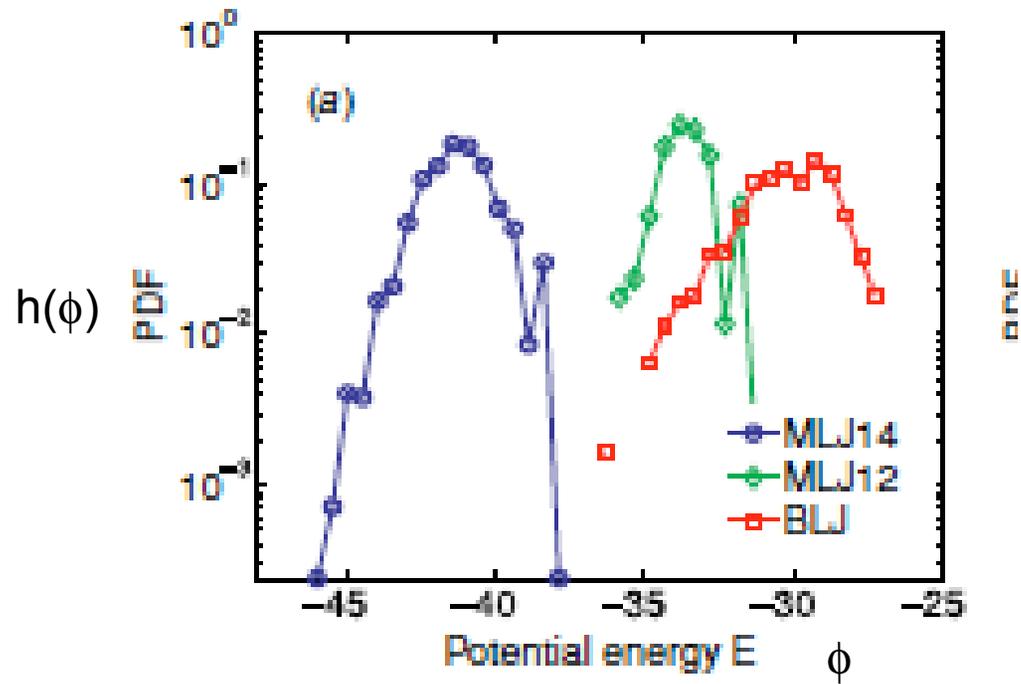
Here  $\sigma(\phi)$  is non-negative function of  $\phi$ . The density of ISs , $h(\phi)$ , is zero except when:

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



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

## Lennard-Jones PELs



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

## Geometrical features of the landscape (contd.)

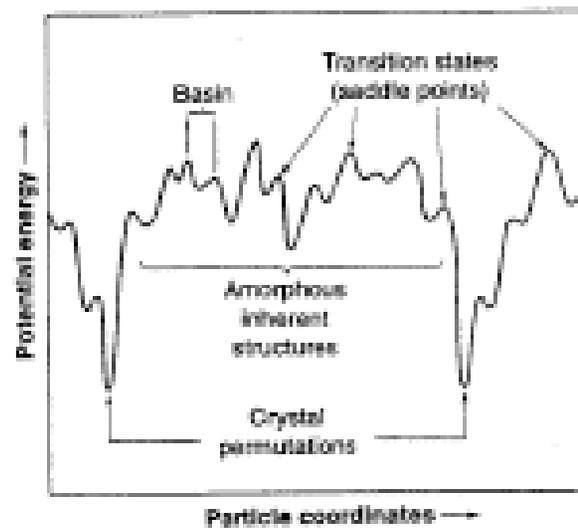
### 3. Basins:

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  $\Omega$  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

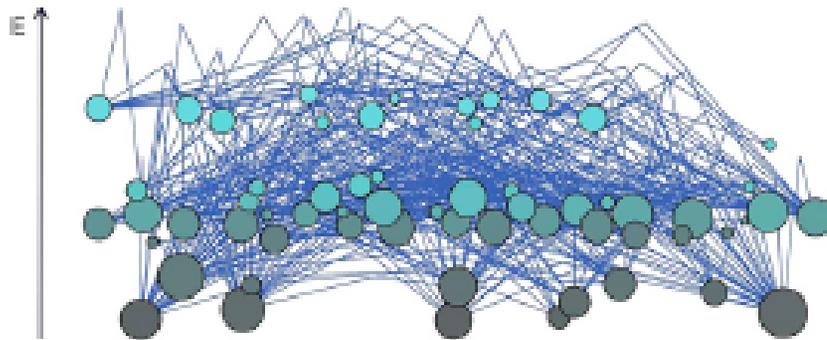
Landscape as a network (nodes and links).

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

Topological measure:

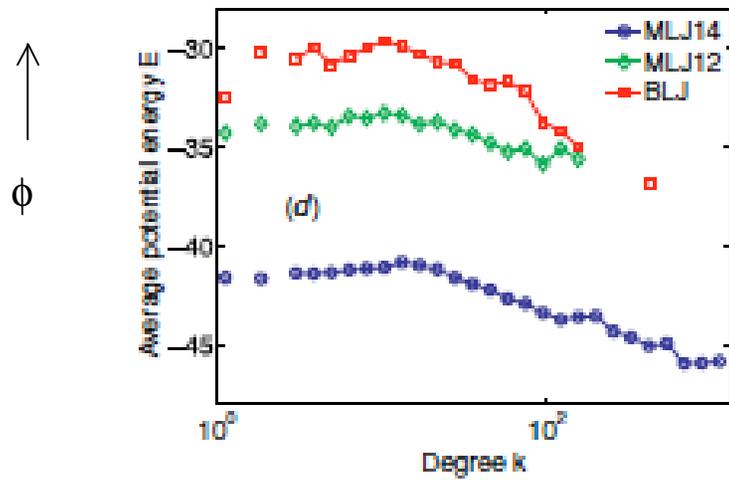
- **Degree (k) of connectivity of a node** is the number of nodes directly linked to the node under consideration.

## Lennard-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 tend to be 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  $X' \equiv \{X, V\}$ . 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 of either the stable or an unstable crystal.
- 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:

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

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

- Since, from equipartition theorem,

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

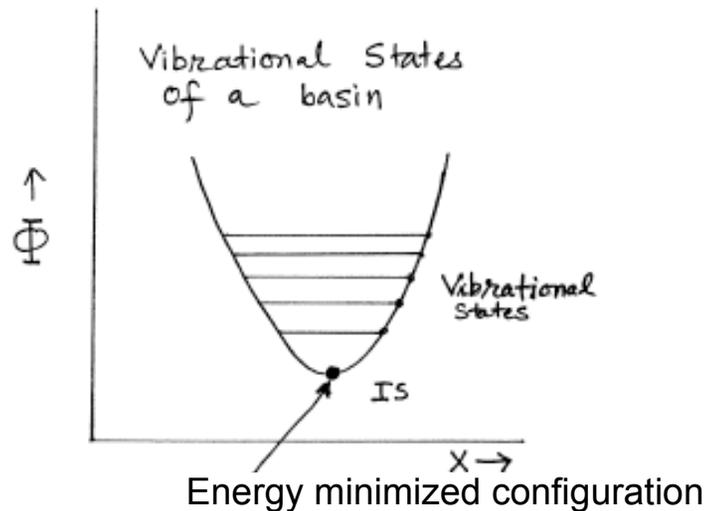
It follows that  $U(X, V, T) = \Phi(X) + (3/2) N k_B T$  .

Similarly, the enthalpy  $H(X', P, T) = \Phi(X) + PV + (3/2) N k_B T$ .

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 of a basin can be calculated from the knowledge of the basin shape (which determines the vibrational frequency,  $\nu$ ) and the basin depth.



## Configurational states of a landscape:

- The inherent structure is the only non-vibrational configuration (the energy minimized configuration) 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

- Key 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 has two parts
  - = Vibrational + Configurational
  - The configurational part originates from ISs.
  - A key advantage of the landscape approach lies in the separation of the vibrational and inherent contributions.
- Degree of connectivity of ISs increases with the depth of IS.  
Deep lying ISs act as hubs in the landscape network.