Selected Features of Potential Energy Landscapes and Their Inherent Structures

Lecture delivered December 11, 2003 for ChE 536

Frank H. Stillinger

Department of Chemistry

Princeton Univesity

Potential Energy/Enthalpy Functions for Many-Particle Systems

- For particle i, let $\mathbf{x}_i$ denote the 3 coordinates for position, plus orientation, and intramolecular deformation, if any. This requires $3+\eta$ coordinates ($\eta \geq 0$).

- Potential energy of interaction for N particles, confined to fixed volume V:

$$\Phi(\mathbf{x}_1...\mathbf{x}_N) = \sum_{i=1}^{N} v_1(\mathbf{x}_i) + \sum_{i<j} v_2(\mathbf{x}_i,\mathbf{x}_j) + \sum_{i<j<k} v_3(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x}_k) + ... \quad .$$

  This normally represents the electronic ground-state energy surface ("energy landscape").

- The intramolecular deformation energy for an isolated particle has been represented by $v_1(\mathbf{x})$. Pair (v_2), triplet (v_3), ... terms represent dispersion attractions, short-distance repulsions, multipole interactions, hydrogen bonds, etc.

- Configuration space dimension for N particles is $(3+\eta)N$.

- General features of Φ:
    (a) diverges to $+\infty$ when any two nuclei approach zero distance;
    (b) symmetric under interchange of identical particles;
    (c) Φ is continuous and at least twice differentiable away from nuclear coincidences;
    (d) for uncharged particles, Φ is bounded below by $-KN$, where K is independent of N;
    (e) Φ reduces to v_1 sum when all particles are widely separated;
    (f) if the boundaries are remote, Φ possesses translational and rotational symmetry;
    (g) in a large system, local rearrangements change Φ only by $O(1)$, not $O(N)$.

- Extension to constant-pressure (isobaric) conditions ($p>0$):
  Append volume V as another configurational coordinate [configuration space dimension increases to $(3+\eta)N+1$]. Introduce "potential enthalpy" function Ψ,

$$\Psi(\mathbf{x}_1...\mathbf{x}_N,V) = \Phi(\mathbf{x}_1...\mathbf{x}_N,V) + pV \quad .$$

Configuration Space Attrition by Particle Repulsive Cores

- Total configuration space content for point particles: V^N.

- Total configuration space content for molecules: $(V \prod_{\xi=1}^{\eta} l_\xi)^N$;

  l_ξ =measure for ξ-th internal degree of freedom.

- Estimate close-encounter strong repulsions as rigid sphere interactions with collision diameter a.

- Non-overlap condition on rigid spheres reduces available configuration space by attrition factor A. Calculate A using non-ideal entropy for rigid spheres:

  $$A = \exp[(S - S_{ideal})/k_B] \quad .$$

- Scaled particle theory approximation for rigid sphere entropy ($y = \pi a^3 N / 6V$):

  $$\frac{\pi p a^3}{6k_B T} = \frac{y(1 + y + y^2)}{(1-y)^3}$$

  [Reiss, Frisch, and Lebowitz, J. Chem. Phys. **31**, 369 (1959)] ;

  $$\frac{S - S_{ideal}}{Nk_B} = \ln(1-y) + \frac{3}{2}\left[1 - \frac{1}{(1-y)^2}\right] \quad .$$

- Numerical values of attrition factor at half close-packing [$y = \pi/(6 \cdot 2^{1/2}) \cong 0.3702$]:

 $$A \cong \exp(-2744) \cong 10^{-1192} \qquad\qquad (N{=}1000) ,$$

  $$A \cong \exp(-1.653 \times 10^{24}) \cong 10^{-7.178 \times 10^{23}} \qquad (N = N_A \cong 6.022 \times 10^{23}) .$$

- Attenuated configuration space is connected, but tortuous!

Steepest-Descent Mapping, Inherent Structures, Landscape Basins

- Any point in the configuration space can be connected to (mapped onto) a relative minimum of the potential energy function $\Phi(\mathbf{x}_1...\mathbf{x}_N)$ by steepest descent. These minima are called inherent structures (IS's).

- Each IS is contained in its own landscape "basin", the set of all configurations that map to that IS by steepest descent.

- Number of basins for large N is asymptotically equal to $N!\exp(\alpha N)$, where $\alpha > 0$.

- Span of Φ values for the IS's is $O(N)$.

- Each basin boundary contains $O(N)$ transition states (simple saddle points of Φ).

- Elementary interbasin transitions are:
  (a) localized, *i.e.* involve shifts of $O(1)$ particles;
  (b) seldom purely permutational.

- Transition state barriers can be arbitrarily small in the "amorphous" region of configuration space. These produce "quantized 2-level systems in low-T glasses.

- Each of the previous statements has an analogous version for the constant-pressure (isobaric) circumstance, where the potential enthalpy $\Psi(\mathbf{x}_1...\mathbf{x}_N, V)$ provides the multidimensional landscape.

Schematic plot of potential energy landscape
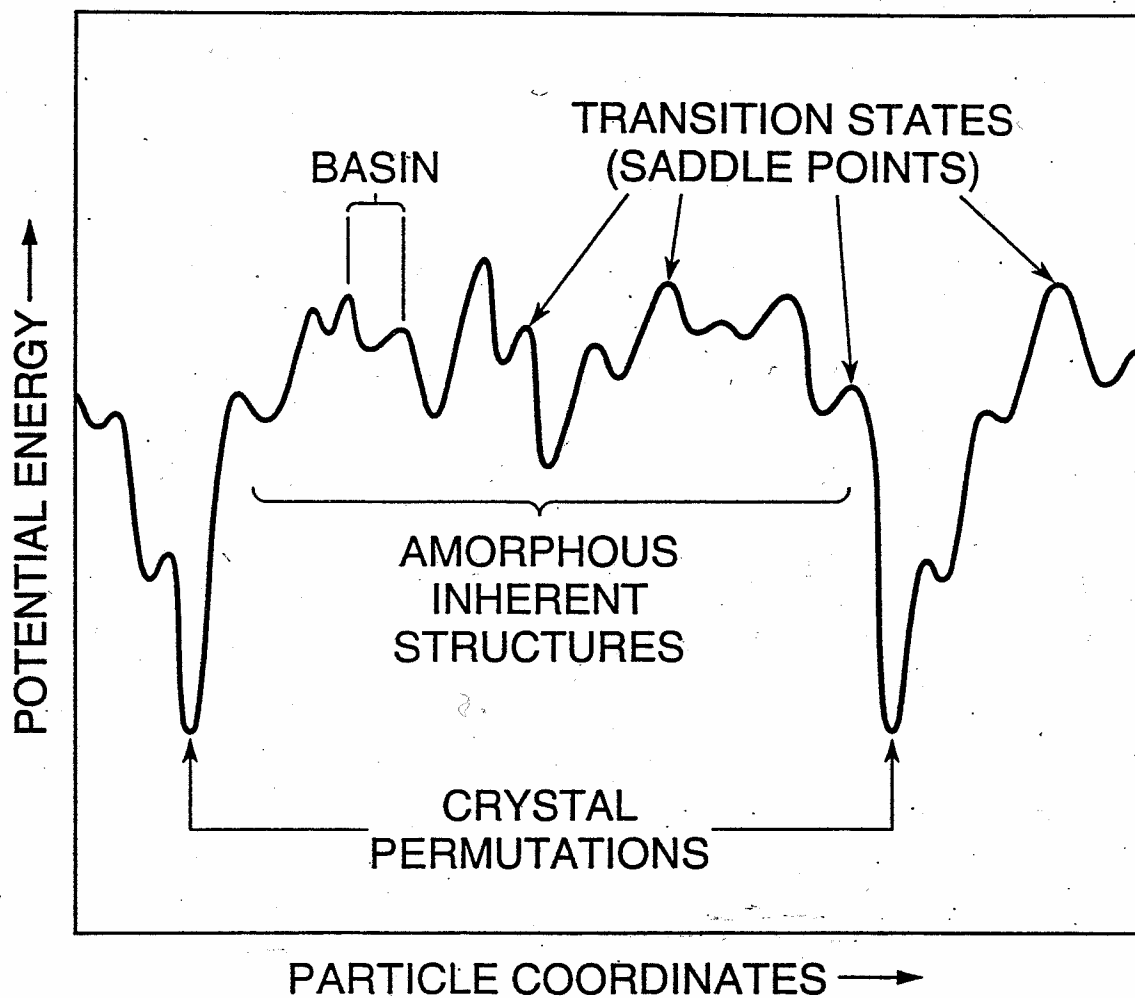
Partition Function Transformation, Constant Volume Conditions

- Classical canonical partition function ($\beta = 1/k_B T$):

$$Q_N(\beta, V) = [N! \Lambda^N(\beta)]^{-1} \int d\mathbf{x}_1 ... \int d\mathbf{x}_N \exp[-\beta \Phi(\mathbf{x}_1 ... \mathbf{x}_N)] \equiv \exp(-\beta F) \ ;$$

  F is the Helmholtz free energy, Λ is the result of momentum integrations.

- Express Q_N as a sum of integrals over distinguishable (permutationally unrelated) basins B_l:

$$Q_N = \Lambda^{-N} \sum_l \exp(-\beta \Phi_l) \int_{B_l} d\mathbf{x}_1 ... \int d\mathbf{x}_N \exp\{-\beta[\Phi(\mathbf{x}_1 ... \mathbf{x}_N) - \Phi_l]\} \ ,$$

  where Φ_l is the potential energy at the basin bottom (the IS).

- Classify IS's by their value of $\varphi = \Phi/N$. The density of distinguishable IS's according to the intensive depth parameter φ for large systems has the exponential form:

$$\exp[N \sigma(\varphi)] \ .$$

- Define $N f_v(\beta, \varphi)$ to be the mean intrabasin vibrational free energy (including Λ^{-N}) for basins with depths in the immediate vicinity of φ.

- Re-express Q_N as a one-dimensional integral over φ:

$$Q_N = \int d\varphi \exp\{N[\sigma(\varphi) - \beta\varphi - \beta f_v(\beta, \varphi)]\} \ .$$

- For large N, the integral is dominated by the neighborhood of the integrand's maximum at $\varphi = \varphi^*(\beta)$. Therefore, the Helmholtz free energy per particle becomes:

$$\beta F / N = \beta\varphi^* + \beta f_v(\beta, \varphi^*) - \sigma(\varphi^*) \ .$$

- $\varphi^*(\beta)$ locates the basins most probably occupied at the given temperature; it is determined by the variational condition:

$$\sigma'(\varphi^*) = \beta[1 + (\partial f_v / \partial \varphi)_{\varphi = \varphi^*}] \ .$$

Intrabasin Vibrational Partition Functions, Constant Volume Conditions

- The classical partition function for a specific basin B_t has the form:

$$\Lambda^{-N} \int_{B_t} d\mathbf{x}_1 ... \int d\mathbf{x}_N \exp[-\beta \Delta_t \Phi(\mathbf{x}_1 ... \mathbf{x}_N)] \equiv \exp[-N\beta f^{(t)}(\beta)] \ ,$$

  where $\Delta_t \Phi$ is the system's potential energy measured from the basin bottom, *i.e.* from the IS. The free energy of vibrational motion restricted to B_t is $Nf^{(t)}(\beta)$.

- Define a mean basin-depth-dependent vibrational free energy $Nf_v(\beta, \varphi)$ to be an average over all basins that have IS potential energies in the narrow range $N(\varphi \pm \delta\varphi)$:

$$\exp[-N\beta f_v(\beta, \varphi)] = \left\langle \exp[-N\beta f^{(t)}(\beta)] \right\rangle_{\varphi \pm \delta\varphi} \ .$$

- $f_v(\beta, \varphi)$ will be essentially harmonic at low temperature, but will contain strong anharmonic contributions at high temperature.

Partition Function Transformations, Constant Pressure Conditions

- Classical isothermal-isobaric partition function ($\beta = 1/k_B T$):

$$\hat{Q}_N(\beta, p) = [N! \Lambda^N(\beta) \lambda_V(\beta)]^{-1} \int d\mathbf{x}_1 ... \int d\mathbf{x}_N \int_0^\infty dV \exp[-\beta \Psi(\mathbf{x}_1 ... \mathbf{x}_N, V)] \equiv \exp(-\beta G) ;$$

  G is the Gibbs free energy, Λ and λ_V result from molecule and piston momentum integrals.

- Express $\hat{Q}_N$ as a sum of integrals over distinguishable (permutationally unrelated) basins $\hat{B}_t$:

$$\hat{Q}_N = \Lambda^{-N} \lambda_V^{-1} \sum_t \exp(-\beta \Psi_t) \int_{\hat{B}_t} d\mathbf{x}_1 ... \int d\mathbf{x}_N \int dV \exp\{-\beta[\Psi(\mathbf{x}_1 ... \mathbf{x}_N, V) - \Psi_t]\} ,$$

  where Ψ_t is the potential enthalpy at the basin bottom (the IS).

- Classify IS's by their value of $\psi = \Psi/N$. The density of distinguishable IS's according to the intensive depth parameter ψ for large systems has an exponential form:

$$\exp[N \hat{\sigma}(\psi)] .$$

- Define $N \hat{f}_v(\beta, \psi)$ to be the mean intrabasin vibrational free energy (including $\Lambda^{-N} \lambda_V^{-1}$) for basins with depths in the immediate vicinity of ψ.

- Re-express $\hat{Q}_N$ as a one-dimensional integral over ψ:

$$\hat{Q}_N = \int d\psi \exp\{N[\hat{\sigma}(\psi) - \beta\psi - \beta\hat{f}_v(\beta, \psi)]\} .$$

- For large N, the integral is dominated by the neighborhood of the integrand's maximum at $\psi = \psi^*(\beta)$. Therefore, the Gibbs free energy per particle becomes:
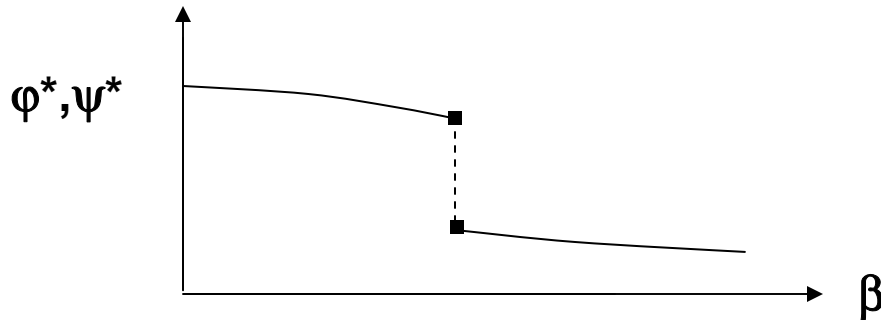
$$\beta G / N = \beta\psi^* + \beta\hat{f}_v(\beta, \psi^*) - \hat{\sigma}(\psi^*) .$$

- $\psi^*(\beta)$ locates the basins most probably occupied at the given temperature and pressure; it is determined by the variational condition:

$$\hat{\sigma}'(\psi^*) = \beta[1 + (\partial\hat{f}_v / \partial\psi)_{\psi=\psi^*}] .$$

Metastable States Modification

- First-order phase transitions (crystal/liquid, liquid/vapor, etc.) involve discontinuities in $\varphi^*(\beta)$, $\psi^*(\beta)$:

- These represent switches from one dominant φ or ψ integral maximum to another, resulting from sudden shifts in population of inhabited landscape basins.

- To avoid these shifts, and to permit metastable extensions of the Helmholtz and Gibbs free energy expressions, separate all basins into distinct subsets corresponding to the IS patterns contributing to the respective phases. Enumeration functions σ, $\hat{\sigma}$ and vibrational free energy functions f_v and $\hat{f}_v$ can then be separately defined for each basin subset.

- **Supercooled liquid case**: Divide basins according to whether or not the IS's contain crystalline regions at least large enough to nucleate freezing. Those that do not are "amorphous IS's", which determine liquid-state properties, whether in equilibrium or in supercooling.

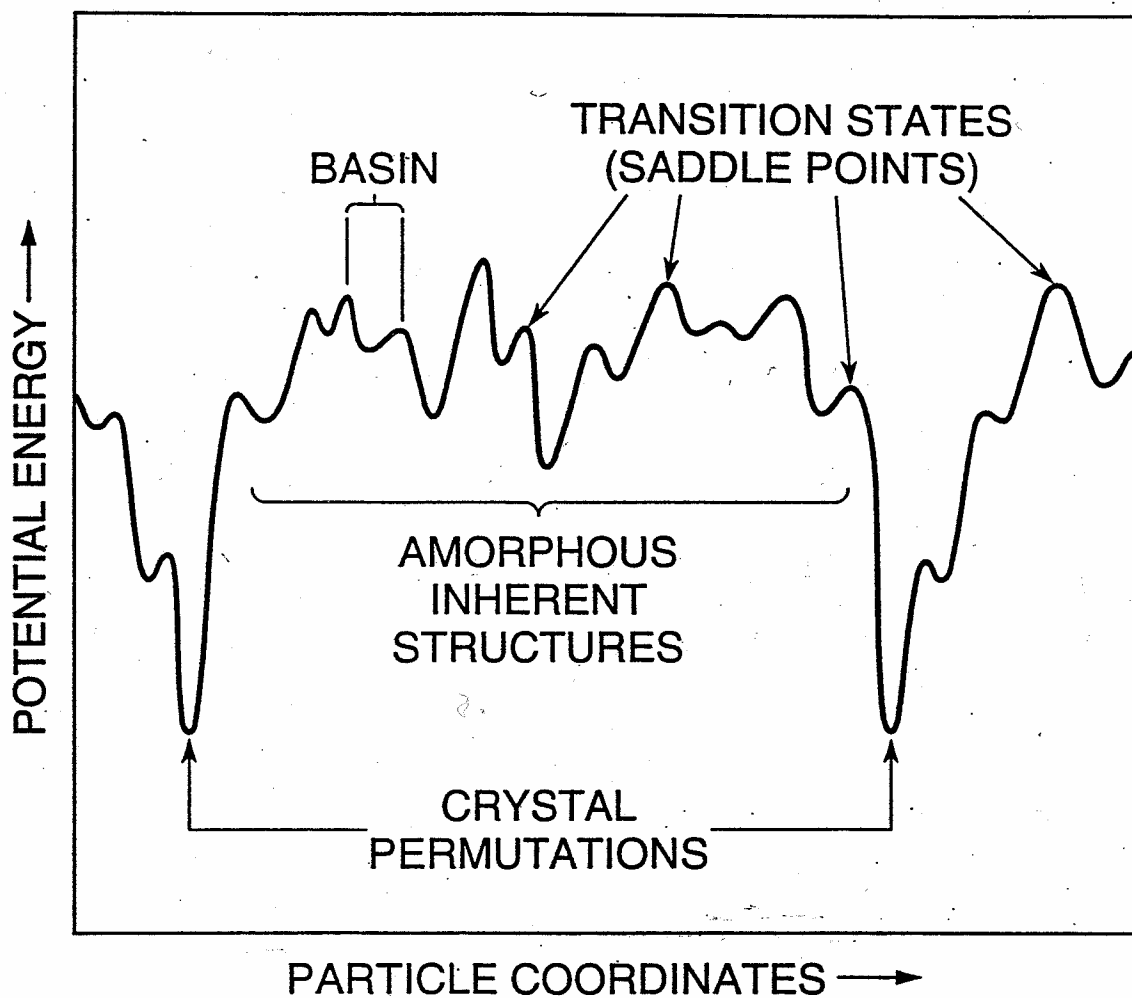- Free energy expressions (subscript a denotes amorphous basin subset):

$$\beta F_a / N = \beta\varphi_a^* + \beta f_{av}(\beta, \varphi_a^*) - \sigma_a(\varphi_a^*),$$

$$\beta G_a / N = \beta\psi_a^* + \beta\hat{f}_{av}(\beta, \psi_a^*) - \hat{\sigma}_a(\psi_a^*),$$

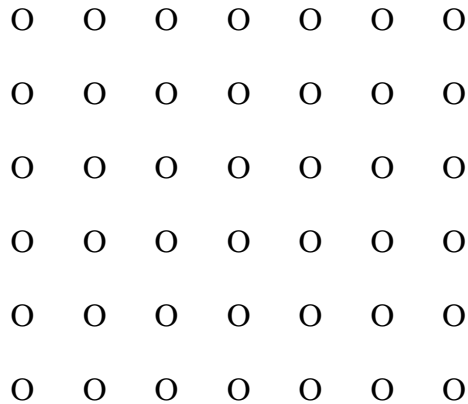where φ_a^*, ψ_a^* are the integrand maxima in this restricted format.

- These free energy expressions lose relevance below a glass transition temperature T_g.

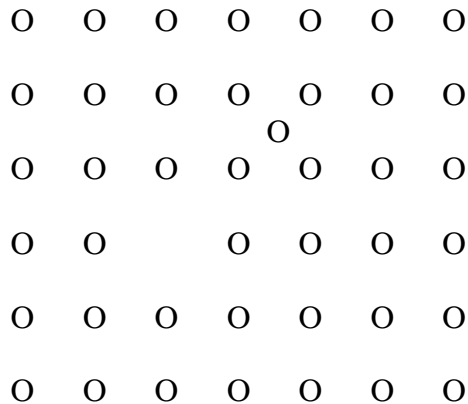Potential energy landscape: projection for distinct metastable states

Interbasin Transitions: Excitations from the Perfect Crystal

- The absolute Φ or Ψ minimum normally corresponds to a structurally perfect crystal:

$$
\begin{array}{ccccccc}
O & O & O & O & O & O & O \\
O & O & O & O & O & O & O \\
O & O & O & O & O & O & O \\
O & O & O & O & O & O & O \\
O & O & O & O & O & O & O \\
O & O & O & O & O & O & O \\
\end{array}
$$

- Elementary excitations consist of minimal displacement of any one of the N particles to a nearby interstitial site:

$$
\begin{array}{ccccccc}
O & O & O & O & O & O & O \\
O & O & O & O & O & O & O \\
  &   &   &   & O &   &   \\
O & O & O & O & O & O & O \\
O & O &   & O & O & O & O \\
O & O & O & O & O & O & O \\
O & O & O & O & O & O & O \\
\end{array}
$$

- The path from the perfect crystal IS to the vacancy-interstitial configuration requires an energy or enthalpy rise of $O(1)$, and surmounts an intervening barrier also of $O(1)$, located at the basin boundary.

- Number of excitations (and their saddle points) out of the absolute minimum basin is nN, where n is the number of equivalent nearby sites for stable residency of the interstitial.

11

Basin Sampling Kinetics – Rough Estimate

- Similarly to the large-system crystal case, amorphous-structure basins are expected to have $O(N)$ transition states to neighbor basins. These arise from $O(N)$ locations in the IS that can independently rearrange to produce a different IS.

- Number of basins that could be populated (isobaric conditions) $\cong \exp[\hat{\sigma}(\psi_a^*)N]$.
  For the glass-former ortho-terphenyl at its freezing point , experimental calorimetry leads to the estimate:
  $$\hat{\sigma}(\psi_a^*) \cong 6.3 \qquad (T = T_m = 329.35K , \quad p = 1bar) ,$$

  [F.H. Stillinger, J. Phys. Chem. B **102**, 2807-2810 (1998)].

- Crude estimate of interbasin transition rate: $R = N \sec^{-1}$.

- Time required for one mole ($N = N_A = 6.022 \times 10^{23}$) of ortho-terphenyl at its melting point to visit all relevant landscape basins in turn, optimistically assuming no returns until all had been inhabited once ("Poincare recurrence"):

  $$t(Poincare) \cong \exp[\hat{\sigma}(\psi^*)N_A] / R(N_A)$$

  $$\cong \exp[(6.3)(6.022 \times 10^{23})] / [6.022 \times 10^{23} \sec^{-1}]$$

  $$\cong 10^{1.648 \times 10^{24}} \sec$$

  $$\cong 10^{1.648 \times 10^{24}} \text{ millenia .}$$

- Qualitatively similar results apply to isochoric conditions, other materials, other temperatures and pressures.

- **Conclusion:** Macroscopic material systems observed over typical laboratory observation times can only visit a tiny fraction of the basins in their multidimensional landscape.

12

Thermal Equilibrium

Whether in isochoric or isobaric conditions, thermal equilibrium requires particle dynamics only to visit a tiny, but representative, sample of all basins enumerated by $\sigma(\varphi)$ or $\hat{\sigma}(\psi)$ [alternatively $\sigma_a(\varphi)$ or $\hat{\sigma}_a(\psi)$ for metastable supercooled states]. In this respect it is analogous to accurate voter polling prior to an election. The representative basin sampling fails below a glass transition temperature.

General Properties of Landscape Basins
(Isochoric Case)

- Each landscape basin is the locus of all points $\mathbf{R}$ in the multidimensional configuration space that steepest-descent mapping connects to its single local minimum (inherent structure):

$$d\mathbf{R}/ds = -\nabla\Phi(\mathbf{R}) \ , \qquad \mathbf{R} \equiv \mathbf{R}(s=0) \ , \qquad \mathbf{R}(s=+\infty) \equiv \mathbf{R}(IS) \ .$$

- Simple transition states connecting neighboring basins lie in the common boundary, have vanishing gradient ($\nabla\Phi = 0$), and one negative curvature (*i.e.* simple saddle point). These transitions correspond to local rearrangements within the *N*-particle system, and are $O(N)$ in number.

- Higher-order saddles also occur at the interbasin boundaries, with $\nabla\Phi = 0$, and $n > 1$ negative curvatures. These are $O(N^n/n!)$ in number, lie $O(n)$ in energy above the IS, and mostly correspond to *n* independent localized transitions occurring simultaneously.

- Saddles of order 1,2,.... can occur within basin interiors, but have nothing to do with transitions between neighboring IS's. Steepest-descent trajectories emanating from such internal saddles all converge onto the single interior IS.

- Basins are forced by definition to be connected, but may be multiply connected.

- The *N*-body intrabasin "vibrational" displacements that move each particle a modest $O(1)$ distance from its position at the IS, have the effect of moving the multidimensional configuration point an $O(N^{1/2})$ from the IS. For some basins, macroscopic elastic displacements are possible, staying within the same basin, that reach $O(N^{5/6})$. [These results rely on the multidimensional form of Pythagoras' theorem.]

- Small intrabasin deviations from the IS can be described as independent normal modes of the *N*-particle system. In this case Φ can be truncated after quadratic terms in the displacements. Diagonalizing the quadratic form for structureless particles with mass *m*,

$$\Phi = (1/2)\sum_{i=1}^{3N} K_i u_i^2 \ ,$$

leads to normal mode angular frequencies $\omega_i = (K_i/m)^{1/2}$.

14

Melting and Freezing Criteria

- For simple point particles, mean-square vibrational displacements from IS positions in 3-dimensional space can be defined as averages over the populated basins:

$$\left\langle (\Delta \mathbf{r}_j)^2 \right\rangle = \left\langle \left\{ \int\limits_{B_l} d\mathbf{R} (\Delta \mathbf{r}_j)^2 \exp[-\beta \Phi(\mathbf{R})] \right\} \right\rangle \left\langle \int\limits_{Bl} d\mathbf{R} \exp[-\beta \Phi(\mathbf{R})] \right\rangle^{-1}$$

  with a corresponding expression for isobaric (constant pressure) conditions.

- Assuming classical statistics is valid, $\left\langle (\Delta \mathbf{r}_j)^2 \right\rangle \propto T$ at low temperature where the harmonic normal mode approximation is valid.

- If thermally excited defects are negligible, only the perfect-crystal basin needs to be considered below the melting point, *i.e.* basin averaging is unnecessary.

- **Lindemann melting criterion:** The thermodynamic melting point occurs when heating causes the dimensionless ratio of root-mean-square particle displacement to nearest-neighbor crystal spacing l to rise approximately to:

$$\left\langle (\Delta \mathbf{r}_j)^2 \right\rangle^{1/2} / l \cong 0.15 \quad .$$

- Values of the Lindemann ratio determined experimentally (by radiation scattering) are somewhat dependent on crystal structure. However this empirical rule works reasonably well for heavier noble gases, ionic crystals, metals.

- The "one-sided" Lindemann melting criterion contrasts with the "two-sided" thermodynamic criteria for phase transitions (equality of temperature, pressure, and chemical potential in both phases).

- Dimensionless "Lindemann ratios" can be defined for liquids, using the amorphous basin set, and using the pair correlation function first peak to identify l. Available evidence indicates that freezing occurs when cooling of the liquid causes its dimensionless ratio to drop to a critical value:
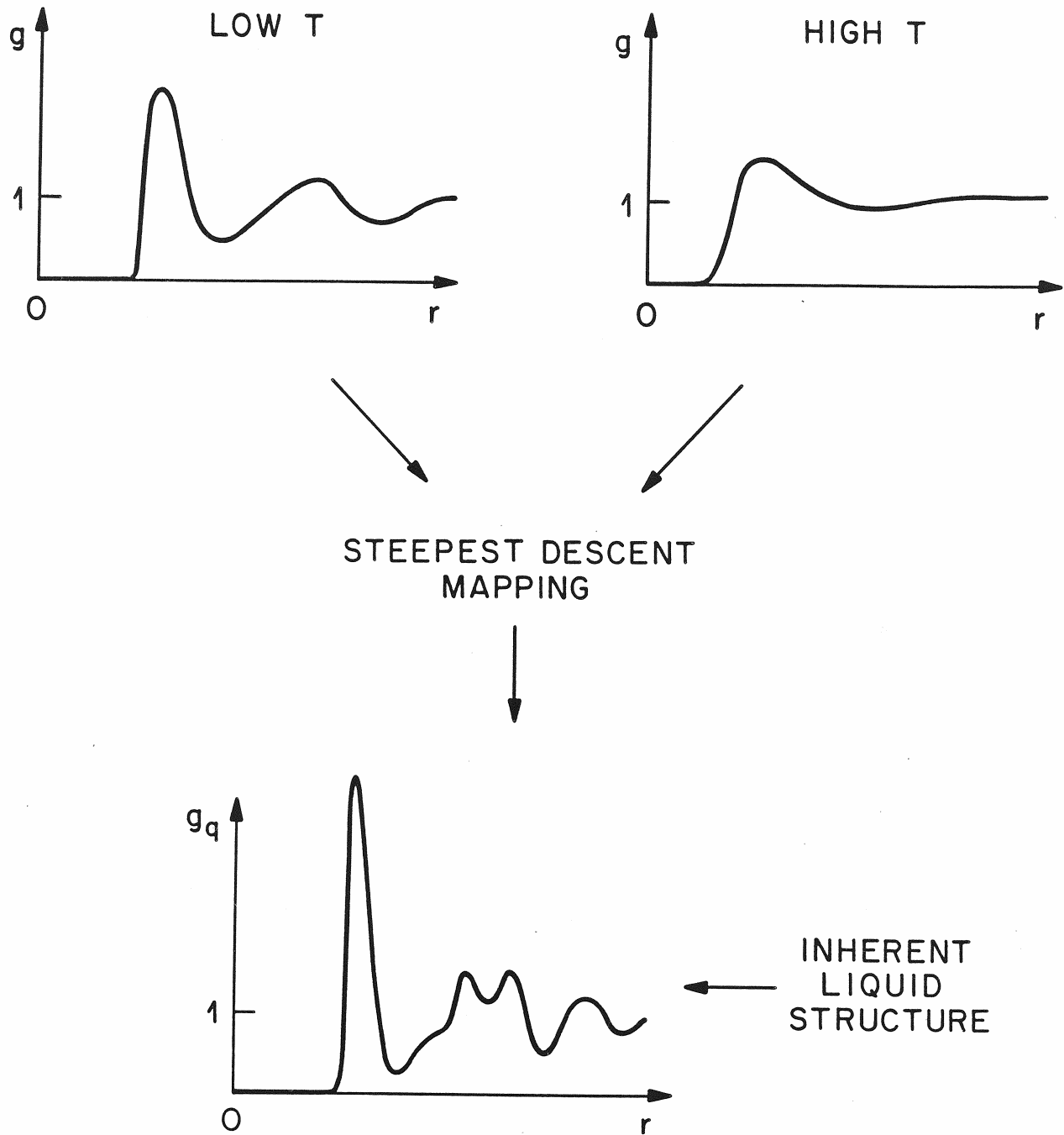
$$\left\langle (\Delta \mathbf{r}_j)^2 \right\rangle / l \cong 0.40 \quad .$$

  This constitutes an "inverse Lindemann" criterion for freezing.

15

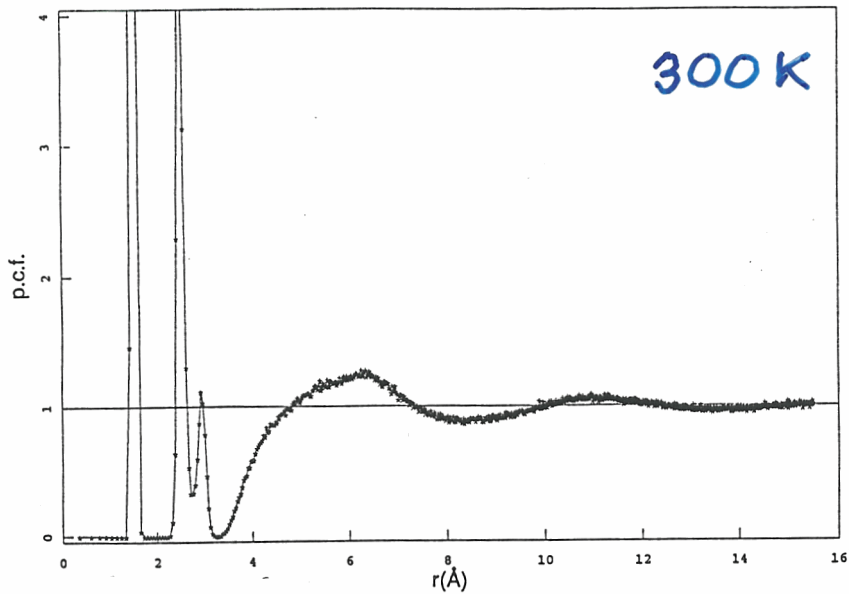Plot of Lindemann ratios *vs.* temperature, crystals and liquids

16
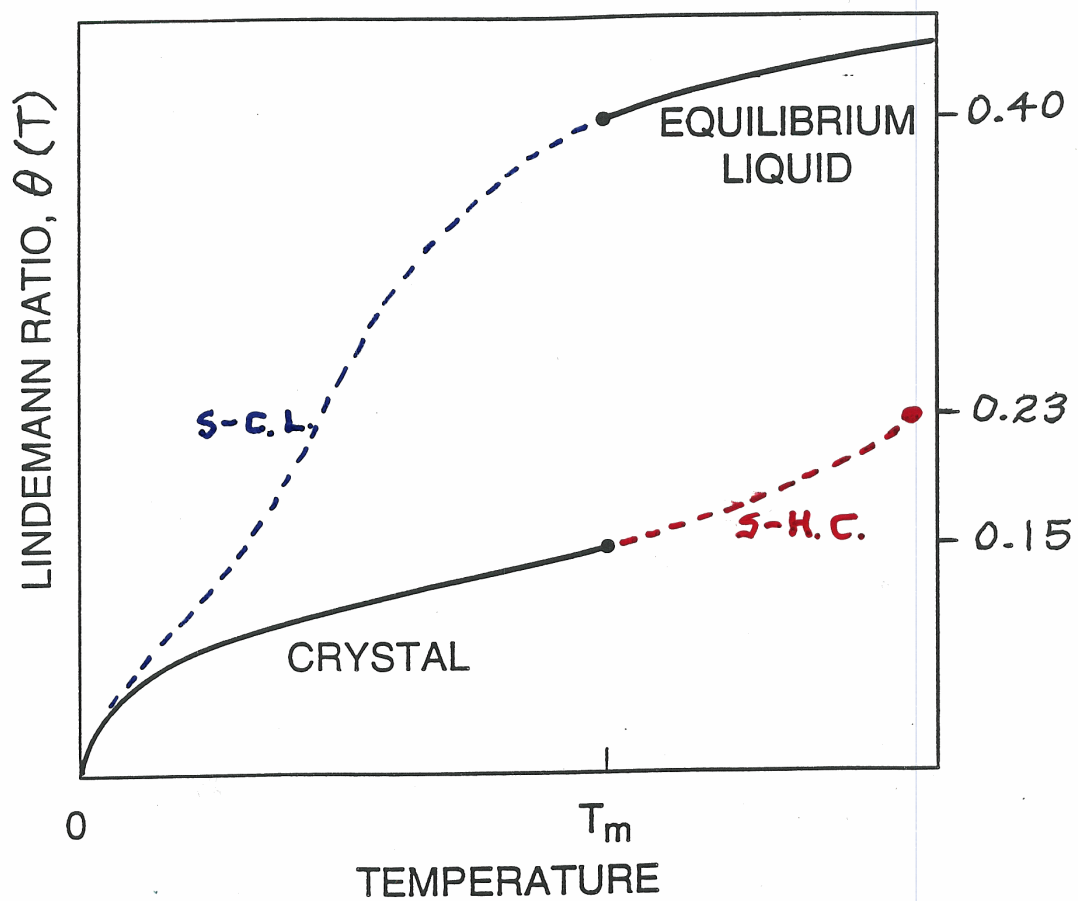
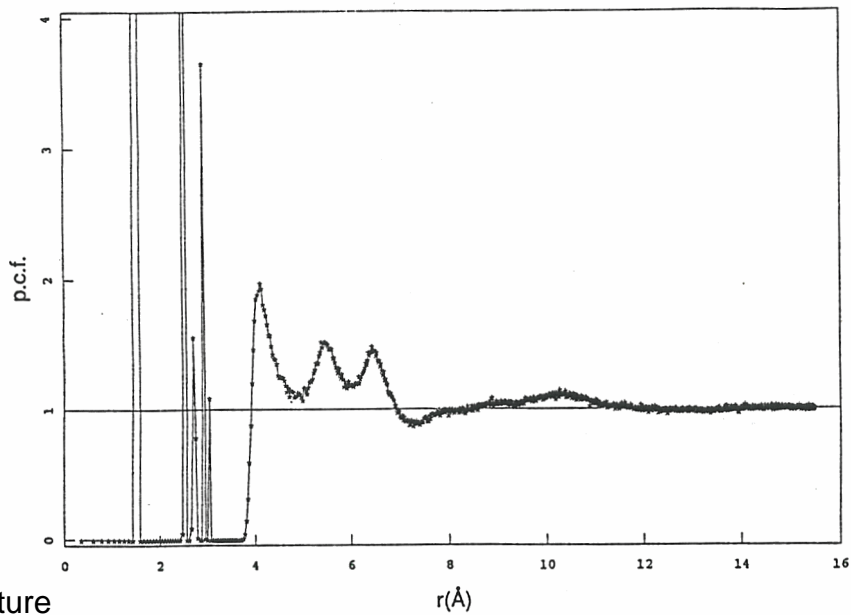# Schematic diagram of s.-d. quenching effect on *g(r)*

Effect of s.-d. quenching on cyclohexane *g(r)*

CYCLOHEXANE,
C—C PAIRS

300 K

S. D. QUENCH

Effect of s.-d. quenching on dihedral angle distribution in *n*-pentane
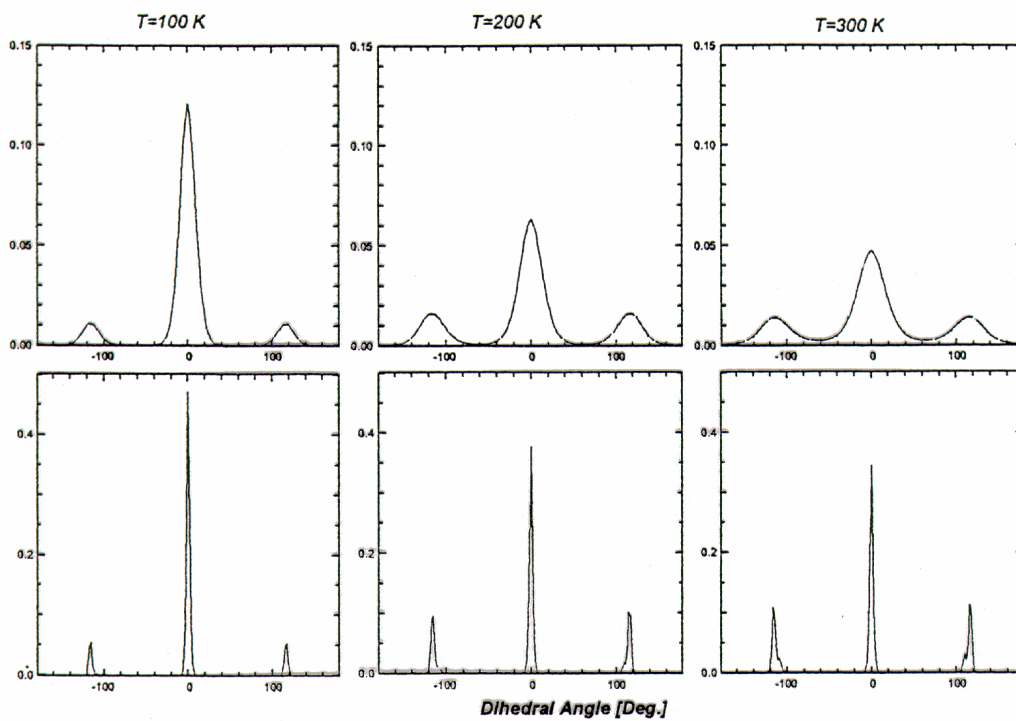

FIG. 2. Dihedral angle distributions in simulations of *n*-pentane. Top row: liquid state at various temperatures; bottom row: Inherent structures obtained from the liquids by steepest descent energy minimization.

Separation of Isothermal Compressibility
(IS + vibrational contributions)

- Isothermal compressibility definition: $\kappa_T = -(\partial \ln V / \partial p)_T$.

- Connection to local order via the pair correlation function (Ornstein and Zernike, 1926):

$$\rho k_B T \kappa_T = 1 + \rho \int d\mathbf{r}[g^{(2)}(r) - 1] \qquad (\rho = N/V) .$$

- Valid for: equilibrium liquids and crystals,
    supercooled liquids,
    non-pairwise-additive interactions,
    classical and quantum statistics.

- Apply isochoric (constant-V) mapping to system configurations to obtain vibration-free pair correlation function $g_{IS}^{(2)}(r)$ for the contributing IS's.

- Add and subtract $g_{IS}^{(2)}(r)$ in the Ornstein-Zernike formula:

$$\rho k_B T \kappa_T = \{1 + \rho \int d\mathbf{r}[g_{IS}^{(2)}(r) - 1]\} + \{\rho \int d\mathbf{r}[g^{(2)}(r) - g_{IS}^{(2)}(r)]\}$$

$$\equiv \rho k_B T[\kappa_T^{(IS)} + \kappa_T^{(vib)}] .$$

- For a structurally perfect crystal, $\kappa_T^{(IS)} \equiv 0$.

- For equilibrium and supercooled liquids, $\kappa_T^{(IS)} > 0$.

- Expressions not applicable to glasses below temperature T_g .

Identification of Contributions to C_V

- Helmholtz free energy per particle in terms of isochoric (constant V) basin properties:

$$\beta F / N = -\sigma(\varphi^*) + \beta\varphi^* + \beta f_v(\beta, \varphi^*) \qquad (\beta = 1/k_B T) \ .$$

- The dominant value of the IS potential energy per particle, $\varphi^*(\beta)$, is determined by the variational criterion:

$$\sigma'[\varphi^*(\beta)] = \beta[1 + (\partial f_v / \partial\varphi)_{\varphi=\varphi^*(\beta)}] \ .$$

- Energy per particle: $\quad \dfrac{E}{N} = \dfrac{\partial \beta F / N}{\partial \beta}$

$$= \varphi^*(\beta) + \left(\frac{\partial \beta f_v(\beta, \varphi)}{\partial \beta}\right)_{\varphi=\varphi^*(\beta)} \ .$$

- Constant-volume heat capacity per particle:

$$\frac{C_V}{Nk_B} = -\beta^2 \frac{dE/N}{d\beta}$$

$$= \left\{-\beta^2 \frac{d\varphi^*}{d\beta}\right\} + \left\{-\beta^2\left[2\frac{\partial f_v}{\partial \beta} + \beta\frac{\partial^2 f_v}{\partial \beta^2}\right]\right\} + \left\{-\beta^2\left[\frac{\partial f_v}{\partial \varphi^*} + \beta\frac{\partial^2 f_v}{\partial \beta \partial \varphi^*}\right]\frac{d\varphi^*}{d\beta}\right\}$$

$$= C_V^{(IS)} + C_V^{(vib)} + C_V^{(IS,vib)} \ .$$

- The cross term $C_V^{(IS,vib)}$ arises from depth dependence of average basin geometry.

Identification of Contributions to C_P

- Gibbs free energy per particle in terms of isobaric (constant p) basin properties:

$$\beta G / N = -\hat{\sigma}(\psi^*) + \beta\psi^* + \beta\hat{f}_v(\beta, \psi^*) \qquad (\beta = 1/k_B T) \ .$$

- The dominant value of the IS potential enthalpy per particle, $\psi^*(\beta)$, is determined by the variational criterion:

$$\hat{\sigma}'[\psi^*(\beta)] = \beta[1 + (\partial \hat{f}_v / \partial \psi)_{\psi = \psi^*(\beta)}] \ .$$

- Enthalpy per particle: $\quad \dfrac{H}{N} = \dfrac{\partial \beta G / N}{\partial \beta}$

$$= \psi^*(\beta) + \left(\frac{\partial \beta \hat{f}_v(\beta, \psi)}{\partial \beta} \right)_{\psi = \psi^*(\beta)} \ .$$

- Constant-pressure heat capacity per particle:

$$\frac{C_p}{N k_B} = -\beta^2 \frac{dH / N}{d\beta}$$

$$= \left\{ -\beta^2 \frac{d\psi^*}{d\beta} \right\} + \left\{ -\beta^2 \left[2\frac{\partial \hat{f}_v}{\partial \beta} + \beta \frac{\partial^2 \hat{f}_v}{\partial \beta^2} \right] \right\} + \left\{ -\beta^2 \left[\frac{\partial \hat{f}_v}{\partial \psi^*} + \beta \frac{\partial^2 \hat{f}_v}{\partial \beta \partial \psi^*} \right] \frac{d\psi^*}{d\beta} \right\}$$

$$= C_p^{(IS)} + C_p^{(vib)} + C_p^{(IS,vib)} \ .$$

- The cross term $C_p^{(IS,vib)}$ arises from depth dependence of average basin geometry.

Resolving Isobaric Thermal Expansion

- Definition: $\alpha_p = (1/V)(\partial V/\partial T)_p$.

- Virial equation of state [additive spherical interactions $v(r)$]:

$$p = \rho k_B T - (2\pi\rho^2/3)\int_0^\infty r^3 v'(r)g^{(2)}(r,T)dr \quad.$$

- Apply $(\partial/\partial T)_p$, rearrange:

$$\alpha_p = (2p - \rho k_B T)^{-1}\left[\rho k_B - (2\pi\rho^2/3)\int_0^\infty r^3 v'(r)(\partial g^{(2)}(r,T)/\partial T)_p\, dr\right] \quad.$$

- Use constant-pressure mapping to potential-enthalpy landscape minima to identify separate basin contributions to $g^{(2)}$. Basin i has occupancy probability $P_i(T)$:

$$g^{(2)}(r,T) = \sum_i P_i g_i^{(2)}(r,T) \quad,$$

$$\left(\frac{\partial g^{(2)}}{\partial T}\right)_p = \sum_i \left(\frac{\partial P_i}{\partial T}\right)_p g_i^{(2)}(r,T) + \sum_i P_i\left(\frac{\partial g_i^{(2)}(r,T)}{\partial T}\right)_p$$

- The two terms in the last expression represent respectively interbasin inherent structural shifts, and intrabasin vibrational shifts. Thus:

$$\alpha_p = \alpha_p^{(IS)} + \alpha_p^{(vib)} \quad.$$

Angell's Strong *vs.* Fragile Glass Formers

Strong limit:

Arrhenius temperature dependence of shear viscosity, mean relaxation time; no discontinuity in C_P across glass transition temperature. [GeO$_2$]

Fragile limit:

Markedly non-Arrhenius temperature dependence of shear viscosity, mean relaxation time; large drop in C_P upon cooling through the glass transition temperature. [OTP]
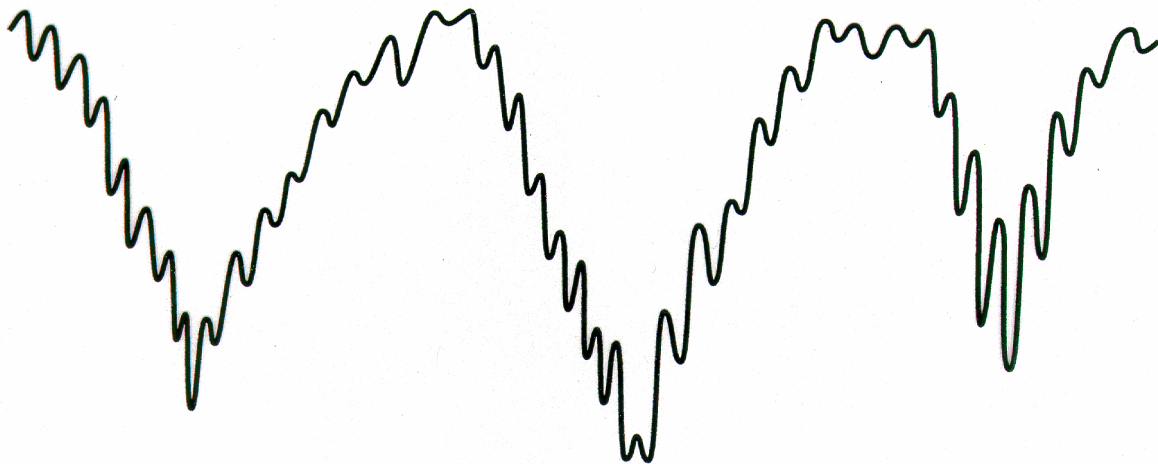
Empirical conclusion:

Thermodynamic and kinetic properties of individual glass-formers are closely correlated with respect to their strong-fragile classification.

Schematic plot of "strong" *vs.* "fragile" landscapes
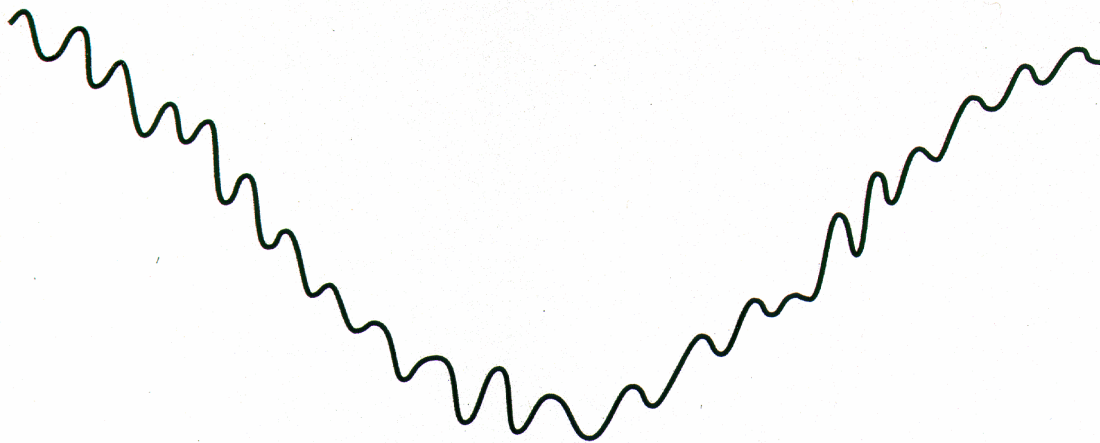
(a) Strong Glass Formers

(b) Fragile Glass Formers

Model energy landscapes confounding strong-fragile correlation idea