Vassiliy Lubchenko

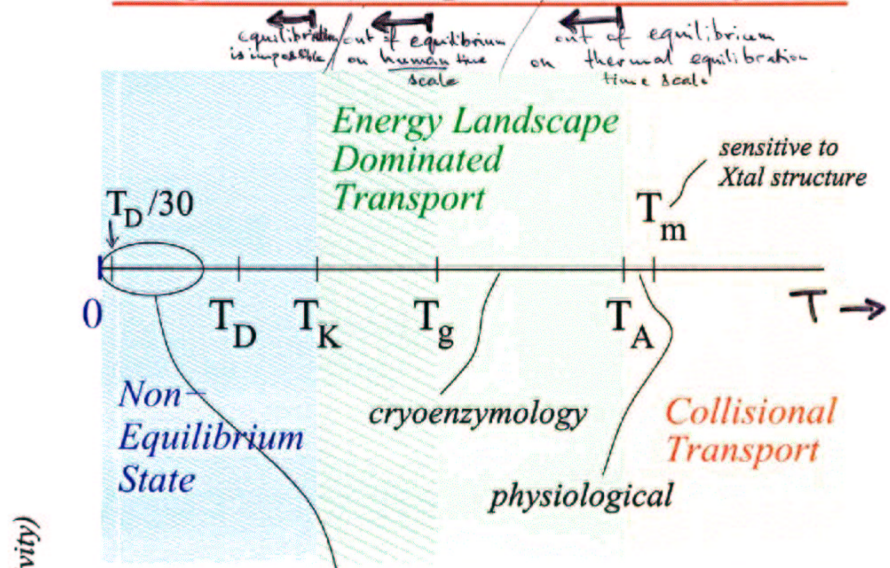
Random First Order Transition Theory: from Quantum Anomalies in Glasses to Control of Protein Conformational Dynamics by Supercooled Solvent

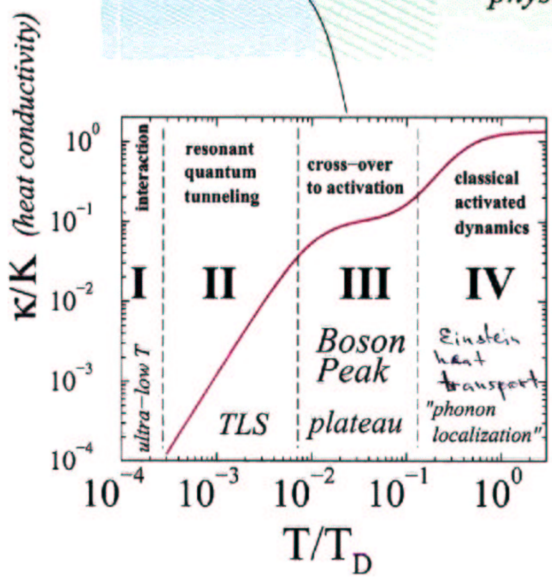
1. The RFOT: microscopic theory of activated transport in supercooled liquids.

2. Low T anomalies in Amorphous Solids.
   a) Intrinsic Quantum Excitations: the origin of the Two Level Systems (TLS).
   b) Boson Peak and Thermal Conductivity Plateau.

3. Nature of Slaving of Protein Motions to Environment. Control of Length and Time Scales of Protein Motions.

Regimes of Liquid/Glass Physics





T_m *melting temperature*

T_A *viscosity catastrophe (dynamical transition)*

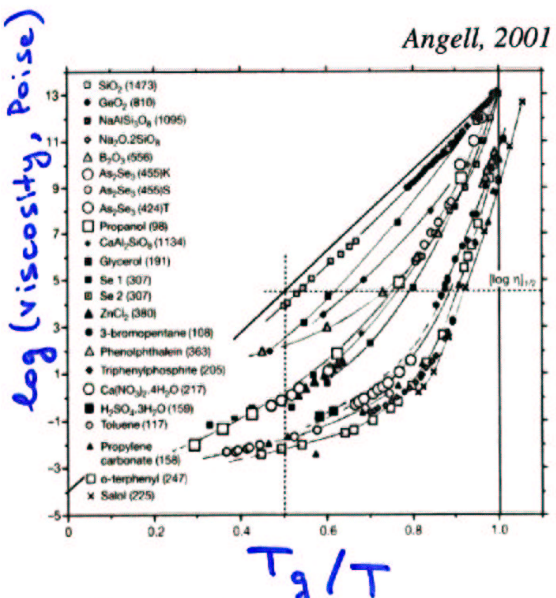
T_g *glass transition*

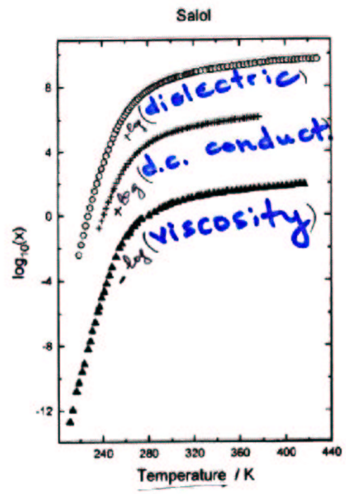
T_K *Kauzmann entropy crisis, $s_c=0$* – "ideal glass transition"

T_D *Debye temperature*

Kinetics
Relaxation Times in Supercooled Liquids

Angell, 2001





F. Stickel at el., 1995

Empirical
Vogel
Fulcher

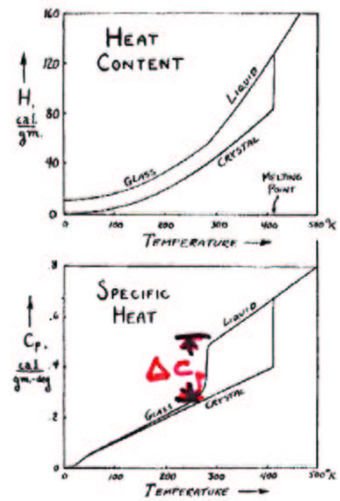
$$\tau = \tau_0 \exp\left(\frac{DT_K}{T-T_K}\right)$$

fragility

D ↑ strong

D ↓ fragile

Thermodynamics
Kauzmann Entropy Crisis 1948



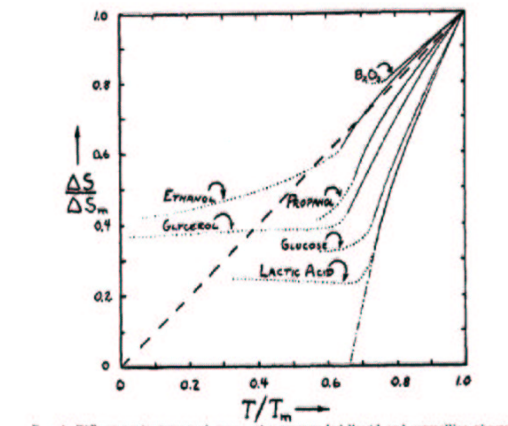
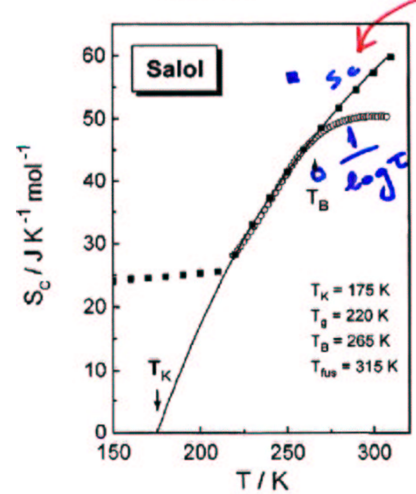


FIG. 4. Differences in entropy between the supercooled liquid and crystalline phases. Abscissa: as in figure 3. Ordinate: difference in entropy expressed as fraction of the entropy of fusion.

Liquid has configurational degrees of freedom!



Oguni (unpublished), Richert & Angell

Configurational Entropy:

$$S_c = S_{liq} - S_{cryst} \simeq$$
$$\simeq \Delta C_p (T - T_K)$$

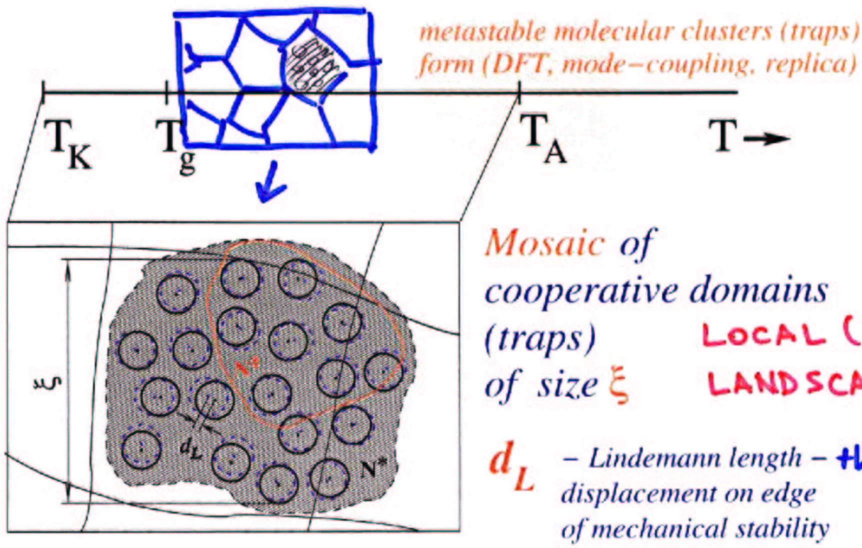
Pattern:

$$\log\tau \propto F^{\ddagger} \propto \frac{1}{S_c}$$

barrier

Kirkpatrick, Thirumalai, Wolynes '89, Xia & Wolynes 2000

The RFOT theory: Mechanism of Activated Transport below T_A



Mosaic of cooperative domains (traps) of size ξ — LOCAL (!) LANDSCAPE

d_L – *Lindemann length* – thermal *displacement on edge of mechanical stability*

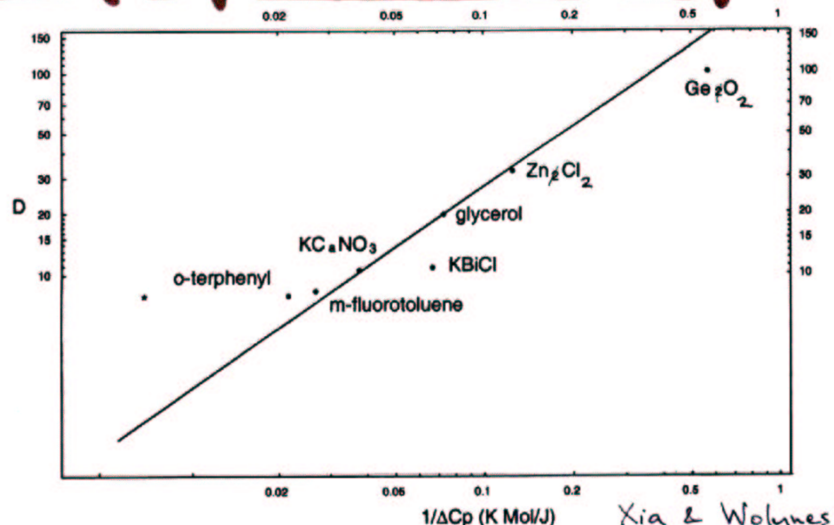
$d_L \simeq 0.1\ a$ ← molecular size

$s_c \simeq \Delta c_p (T - T_K) \simeq 0.78$ at T_g on 1 hour scale

barrier $F^{\ddagger} \propto \frac{1}{s_c} \propto \frac{1}{\Delta c_p (T - T_K)} \Rightarrow D = \frac{32.}{\Delta c_p}$

cooperative length $\xi \propto \frac{1}{(T - T_K)^{2/3}}$, 5 − 6 molecular sizes at T_g

Random First Order Transition Theory: Fragility vs. Heat Capacity Jump



Xia & Wolynes, 2000

fragility → $D = \frac{32R}{\Delta c_p}$ ← heat capacity jump at T_g per moving unit

Vogel Fulcher Law $\tau = \tau_0 e^{\frac{D T_K}{T - T_K}}$

RFOT establishes a connection between kinetics & thermodynamics of supercooled liquids on a constructive footing

Random First Order Transition Theory of Structural Glass Transition

Xia & Wolynes '00

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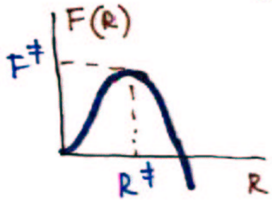
Free Energy profile of replacing a local sol'n of Liquid Free Energy Functional by another:

$$F(R) = 4\pi\,\sigma(R)\,R^2 - \frac{4\pi}{3} R^3\,\tilde{s}_c\,T$$

energy cost to create a domain wall VS. entropic advantage of breaking up into domains of different sol'ns



$\tilde{s}_c$ - configurational entropy

$e^{\tilde{s}_c V}$ - # of soln's per volume V

$\sigma(R) = \sigma_0 \left(\frac{a}{R}\right)^{1/2}$ - curvature dependent surface tension

Villain, '85 RFIM

$10^{17} = \frac{\tau_{exp}}{\tau_0} = e^{\frac{F^\ddagger}{T_g}}$ fixes T_g

$F^\ddagger \propto \frac{1}{s_c} \propto \frac{1}{T - T_k}$ Vogel Fulcher

Low T Anomalies in Glasses

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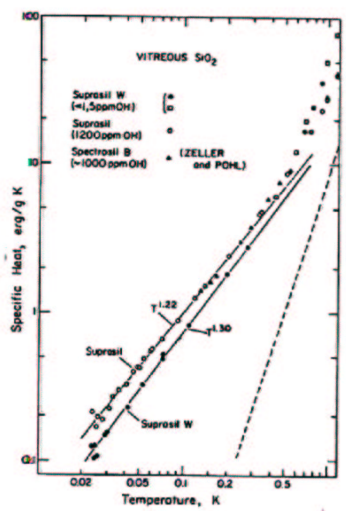

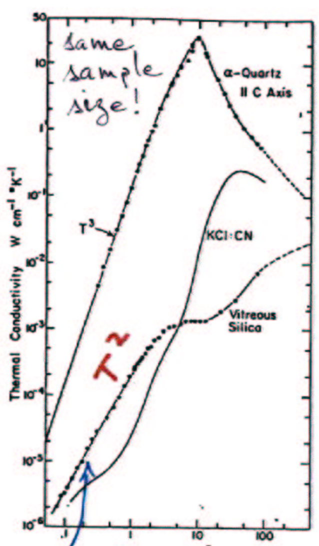

Zeller & Pohl '71

$$c_v \simeq \bar{P}\,T$$

density of states $10^{45\pm1}\ [J^{-1} m^{-3}]$

$$\frac{\ell_{mfp}}{\lambda} \propto \left[\bar{P}\,\frac{g^2}{\rho c_s^2}\right]^{-1}$$

const ~150

assuming kinetic theory $\kappa = \frac{1}{3} c_s\, c_v\, \ell_{mfp}$

g - coupling with phonons ~1eV

$$\mathcal{H} = \frac{\varepsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x + (g\nabla\varphi)\sigma_z$$

Standard Tunneling Model of Two Level Systems

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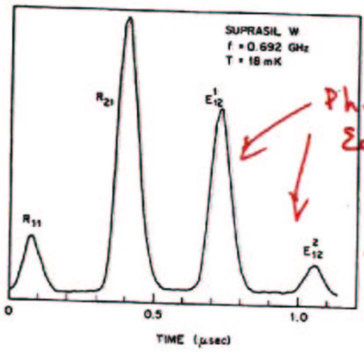
Anderson, Halperin, Varma
Phillips 1972



Phonon Echo

Graebner Golding '78

$$\mathcal{H} = \frac{\varepsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x + (\bar{g}\bar{\nabla}\varphi)\sigma_z$$

elastic strain

$$\mathcal{H}_{ph} = \int d^3r \left[\frac{\pi^2}{2\rho} + \frac{\rho c_s^2}{2}(\nabla\varphi)^2 \right]$$

$$\bar{P} \simeq 10^{45\pm1} \frac{1}{JM^3}$$

density of states

Microscopic Nature ?

Universality in $\frac{\ell_{mfp}}{\lambda} \Rightarrow$ ≃ 150 for all insulating glasses!

$\Rightarrow$ Universality in $\bar{P}\frac{g^2}{\rho c_s^2}$

Freeman & A.C. Anderson '86, Yu & Leggett '88

Mosaic Structure of a Supercooled Liquid & Residual Degrees of Freedom in Glasses below T_g

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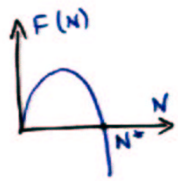
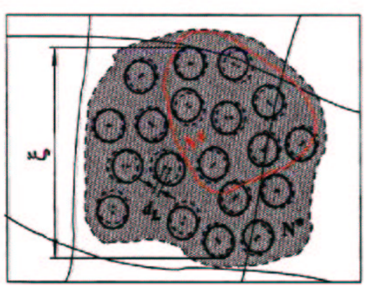
$$F(R) \Rightarrow \boxed{F(N) = \gamma\sqrt{N} - T_g s_c N}$$



$F(N^*) = 0 \Rightarrow N^* \simeq 190$ molecules

$(\xi/a) \simeq 5.8$ $\quad N^* \equiv \left(\frac{\xi}{a}\right)^3, \quad N \equiv \frac{4\pi}{3}\left(\frac{r}{a}\right)^3$



$$\frac{\xi}{a} = \left\{ \frac{\frac{8}{3\sqrt{3\pi}} \log\left(\frac{\tau}{\tau_0}\right)}{\log\left[\left(\frac{a}{d_L}\right)^2 \frac{1}{\pi e}\right]} \right\}^{2/3}$$

d_L - Lindemann length
a - molecular length scale

a liquid-like Degree of Freedom per ~ 200 molecules

Simple Way to interpret molecular scale surface tension at the droplet-droplet interface

Xia + Wolynes → $\sigma_0 = \frac{3}{4}\frac{T}{a^2}\ln\left(\frac{a^2}{d_L^2 \pi e}\right)$

Free energy of monatomic gas:

$$\frac{F}{N} = -\frac{3}{2}T\ln\left[\left(\frac{eV}{N}\right)^{2/3}\frac{mT}{2\pi\hbar^2}\right]$$

Particle in the box of size d_L

$$\frac{1}{2}\frac{\hbar^2}{m}\left(\frac{\pi}{d_L}\right)^2 \simeq T$$

$$\boxed{\frac{V}{N} = a^3}$$

$$\Rightarrow \frac{F}{N} = -\frac{3}{2}T\ln\left(\frac{a^2}{d_L^2}\frac{e^{2/3}\pi}{4}\right)$$

Random Energy Model Argument on Density of States (DOS)

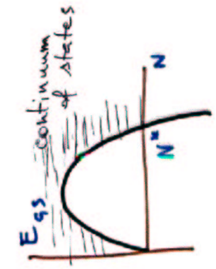
VL + P. Wolynes (7)

$$\Omega_N(E) \propto e^{s_c N - \frac{[E-(T_g s_c N + \gamma\sqrt{N})]^2}{2\delta E^2 N}}$$

density of states of a region of size N + cost of domain wall creation

$\Omega_N(E_{gs}(N)) = 1$ guaranteed lowest energy state

$$\Rightarrow E_{gs}(N) = \gamma\sqrt{N} - T_g s_c N$$



Region of size $N^* = (\xi/a)^3$ has DOS:

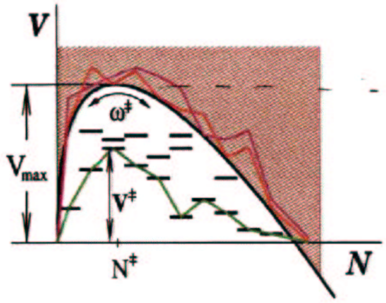
$$n(E) = \frac{1}{T_g}e^{\frac{E}{T_g}}$$

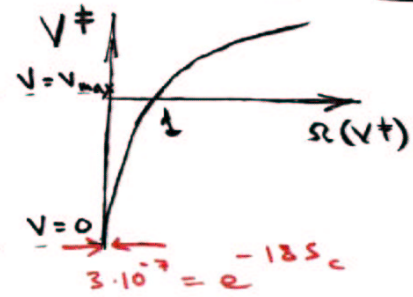
$$\bar{P} = \frac{1}{T_g \xi^3} \sim 10^{45}\frac{1}{JM^3}!$$

Kinetics?

(9)

Lowest Barrier Distribution + Domain Wall Mass





Frozen-in Distribution of Barriers:

$$\boxed{\Omega(V^{\ddagger}) \propto e^{\frac{V - V_{max}}{\sqrt{2} T_g}} = e^{-18 s_c + \frac{V^{\ddagger}}{\sqrt{2} T_g}}}$$

Region larger by 18 molecules than the N^* from static argument has a zero-barrier path!

Domain Wall Mass: $M_w \left(\frac{a}{\tau}\right)^2 = N_w m \left(\frac{d_L}{\tau}\right)^2$

$(M_w / N_w) = (d_L/a)^2 m = 0.01\, m$ per atom!

Barrier Frequency: $\omega^{\ddagger} \simeq 1.6 \left(\frac{a}{\xi}\right) \omega_D$

(10)

Defects' Coupling to Lattice Strain + Universality of Phonon Scattering

$$\mathcal{H} = \int d^3 r \left[\frac{\pi^2}{2\rho} + \rho c_s^2 \frac{(\nabla\varphi)^2}{2} \right] + (\bar{g} \bar{\nabla} \varphi)\, \sigma_z$$

Stability condition at T_g:

$$\langle \rho c_s^2 a^3 (\nabla\varphi)^2 \rangle \simeq \langle \bar{g} \bar{\nabla} \varphi\, \sigma_z \rangle$$

&

$$\langle \rho c_s^2 (\nabla\varphi)^2 a^3 \rangle \simeq T_g \text{ - equipartition}$$

$$\Rightarrow \boxed{g \simeq \sqrt{T_g \rho c_s^2 a^3}}$$

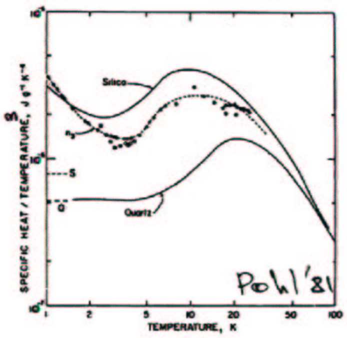
$$\frac{\ell_{mfp}}{\lambda} \sim \left(\frac{\bar{P} g^2}{\rho c_s^2} \right)^{-1} \sim \left(\frac{\xi}{a} \right)^3 \simeq 200$$

is universal!

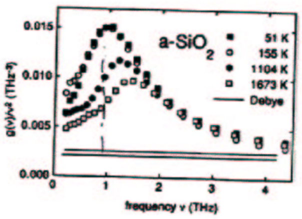
$$\bar{P} \simeq \frac{1}{T_g \xi^3}$$

Warmer T Anomalies

(3)

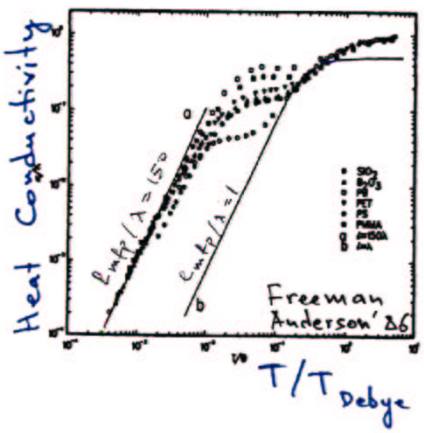


"Boson Peak"



Wischnewsky et al '97

~1 THz in a-Silica



Plateau in Heat Conductivity

$a \Rightarrow \frac{l_{mfp}}{\lambda} \simeq 150$

plateau

$b \Rightarrow \frac{l_{mfp}}{\lambda} \simeq 1$

Mobile Domain Walls Carry Ripples!

(12)

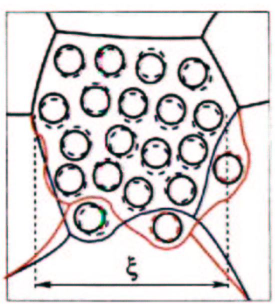
Ripplon Spectrum

VL + P. Wolynes

σ - surface tension coeff

ρ_w - mass density per unit area

ρ_g - density of the (fake) gas inside



Spherical Shell with Gas:

$$\cot\left[\alpha_n\left(\frac{\omega R}{c_g}\right)\right] = \frac{\rho_w}{\rho_g R} - \frac{(l-1)(l+2)}{\omega R^2}\frac{\sigma}{\rho_g R}$$

$l \geq 2$

$$\rho_g \to 0 \Rightarrow \boxed{\omega_l^2 = \frac{9}{8}\frac{\sigma}{\rho_w R^2}(l-1)(l+2)}$$

correction due to $\sigma(R)$ R dependence

$$\boxed{\omega_l \simeq 1.34\,\omega_0 \left(\frac{a}{\xi}\right)^{5/4}\sqrt{\frac{(l-1)(l+2)}{4}}}, \quad l = 2..9$$

$(2l+1)$ degenerate

$\omega_l \simeq 1$ THz for a-Silica

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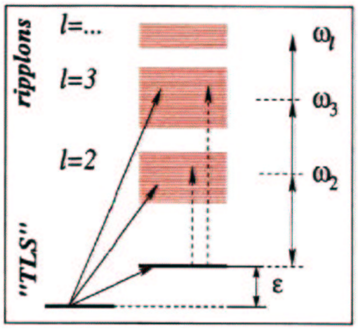
Combined DOS of Structural Transitions + Ripplons



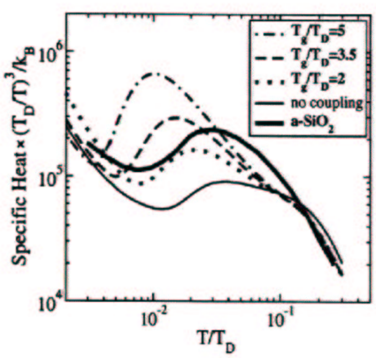
Partition Function:

$$Z_\epsilon = 1 + \sum_{\{n_{\ell m}\}} e^{-\beta(\epsilon + \sum n_{\ell m}\omega_{\ell m})}$$

$$= 1 + e^{-\beta\epsilon} \prod_\ell Z_\ell^{2\ell+1}$$

Heat Capacity per Domain

$$c_\epsilon = \beta^2 \frac{\partial^2 \log Z_\epsilon}{\partial \beta^2}$$



$$\int d\epsilon\, n(\epsilon)\, c_\epsilon$$

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Scattering DOS of Entropic Droplet Excitations

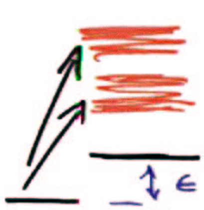
Coupling to phonons:

$g = \rho c_s^2 \int d\vec{s}\, \vec{d}$ the same as TLS transition

$\vec{d}$ - tunneling displacement on droplet's edge

Absorption from Ground State:

$$\rho(\omega) = \int_0 d\epsilon\, \underbrace{n(\epsilon)}_{\frac{1}{T_g \xi^3} e^{-\frac{|\epsilon|}{T_g}}} \sum_{\{n_{\ell m}\}} \delta(\omega - [\epsilon + \sum n_{\ell m}\omega_{\ell m}])$$



$$\rho(\omega) \xrightarrow[\omega \to 0]{} \frac{1}{T_g \xi^3} \quad \text{TLS DOS}$$

Scattering DOS cont'd

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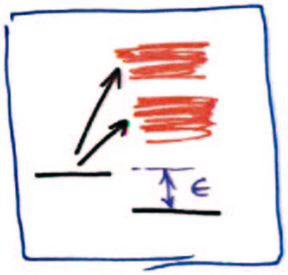
absorption from Excited State:

$$N_E(\omega) = \int_0^E d\epsilon\, n(\epsilon) \sum_{\{n_{em}\}} \delta\left(\omega - \left[\sum_{em} n_{em}\omega_{em} - \epsilon\right]\right)$$



$$\rho_{exc}(\omega, T) = \int_0^\infty dE\, \frac{\partial N_E(\omega)}{\partial E} \frac{2}{1+e^{\beta E}}$$

Phonon's Life time:

$$\tau_\omega^{-1} \simeq \omega \frac{\pi g^2}{\rho c_s^2}\left[\rho(\omega) + \rho_{exc}(\omega)\right]$$

$$\mathcal{H}_{ph} = \sum_k \omega_k a_k^+ a_k + \sum_k \frac{g(k)}{\sqrt{2\omega_k \rho V}} (a_k^+ + a_k)\, \sigma_z$$

Interaction with Phonons Causes Frequency shift + Resonance Broadening

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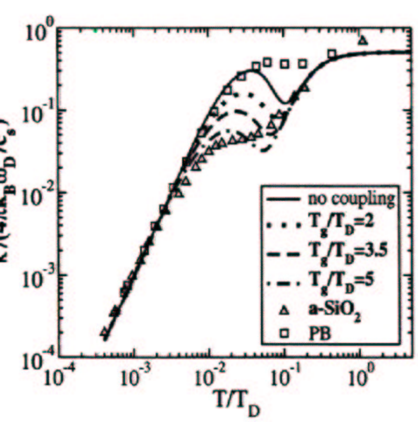
$$\sum_{em} \int d\omega\, (\omega - \omega_{em}) \rightarrow \sum_{em} \int d\omega \frac{\gamma_\omega/\pi}{[\omega - \omega_c(\omega)]^2 + \gamma_\omega^2}$$

$$\gamma_\omega \simeq \frac{3\pi}{2} T_g \left(\frac{\omega}{\omega_D}\right)^3 \text{ – line broadening}$$

$$\omega_c(\omega) = \omega_c - \frac{3}{2} T_g \left(\frac{\omega_c}{\omega_D}\right)^3 P\!\!\int_0^{\omega_c} \frac{d\omega' (\omega'/\omega_c)^3}{\omega' - \omega} \text{ – frequency shift}$$



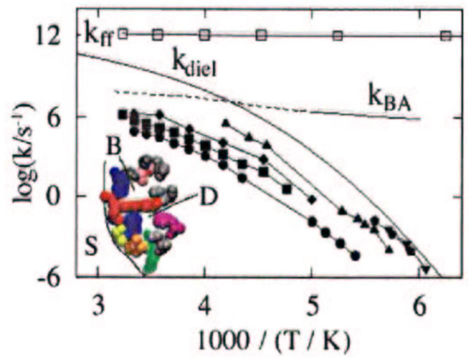
ω_c – cut-off frequency

$$\begin{cases} \omega_c \propto \omega_D \\ \Delta\omega_c \propto T_g \end{cases}$$

plateau's non-universality!

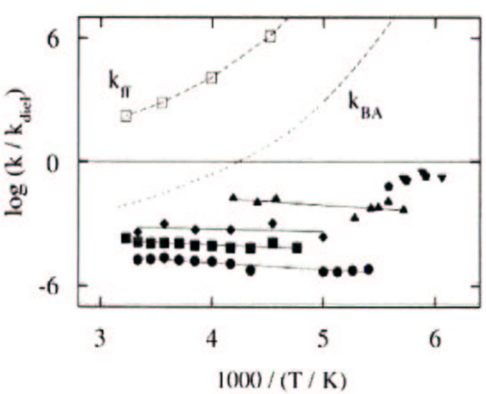
Slaved Relaxation in Myoglobin

H.Frauenfelder et al.



Solvent:

H_2O + glycerol mixture

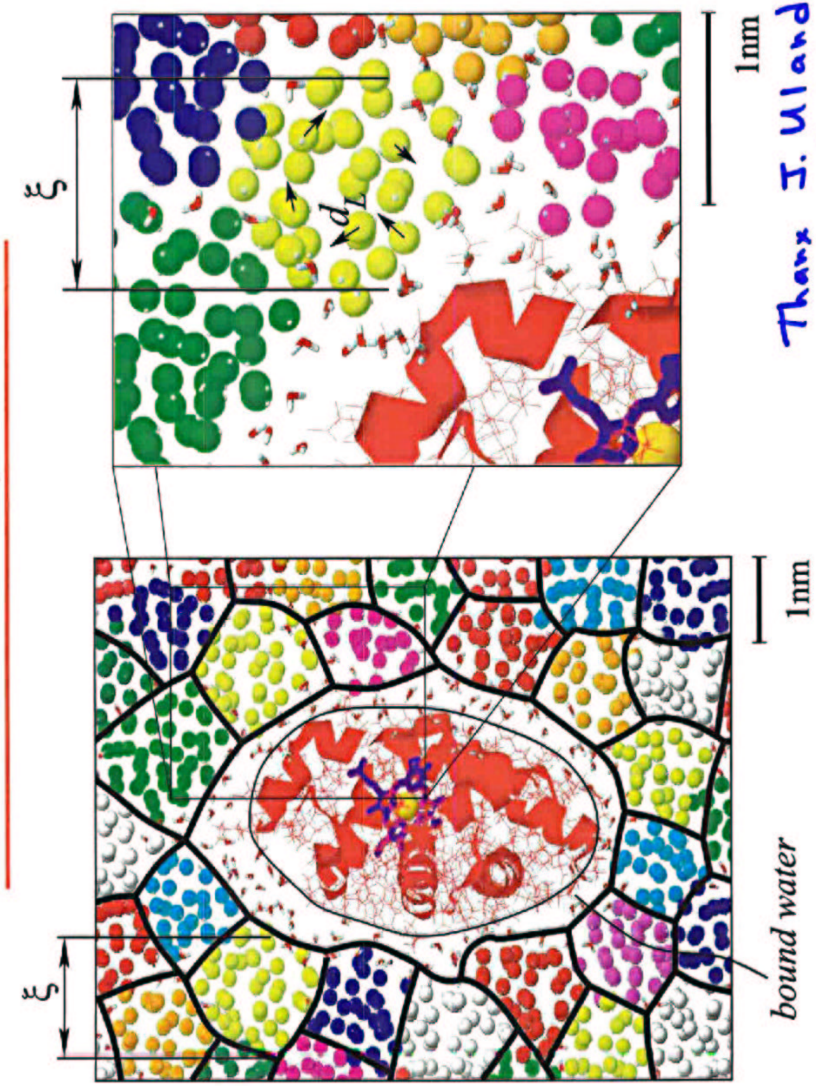


Slaved:

$$\frac{k}{k_{diel}} \simeq \text{const} < 1$$

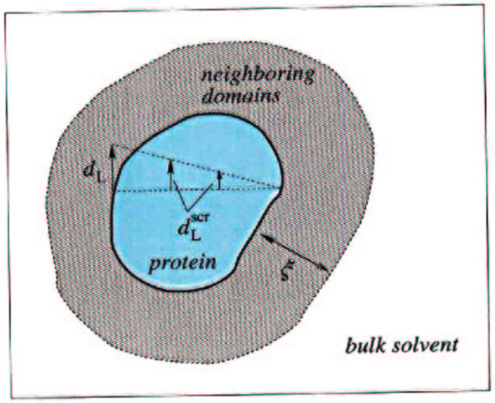
Frauenfelder, VL, Wolynes

Protein in Glassy Solvent



Thanx J. Ulander for help!

Protein subject to Solvent Motions



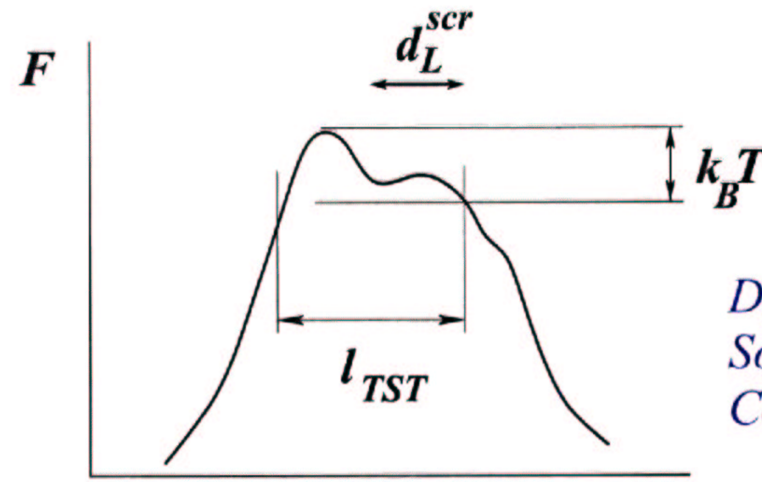
Protein Motions: Transitions between distinct structural States

length scale: d_L^{scr} fragility

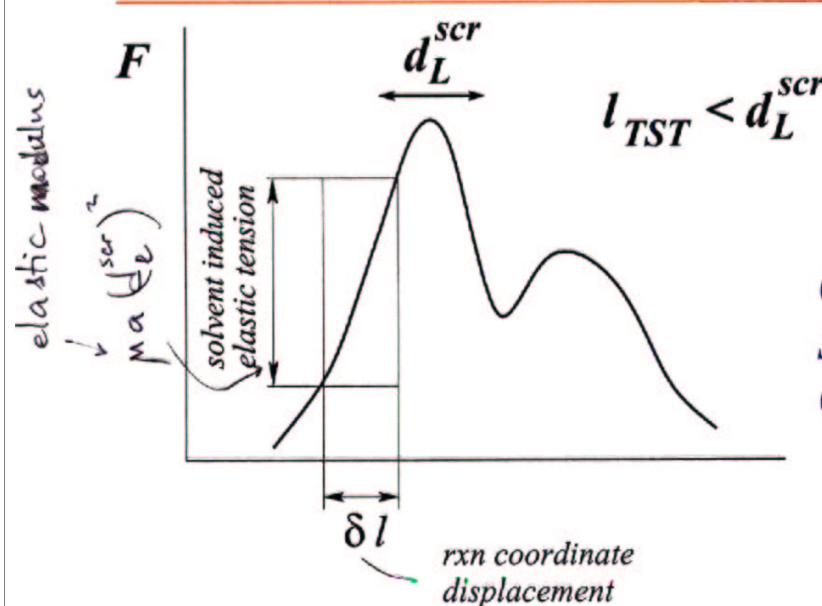
time scale: $\tau = \tau_0 e^{\frac{D_K T_K}{T - T_K}}$ (VF)

effective Diffusion Constant: $D = \frac{(d_L^{scr})^2}{2\tau}$

Diffusive vs. Gated Kinetics

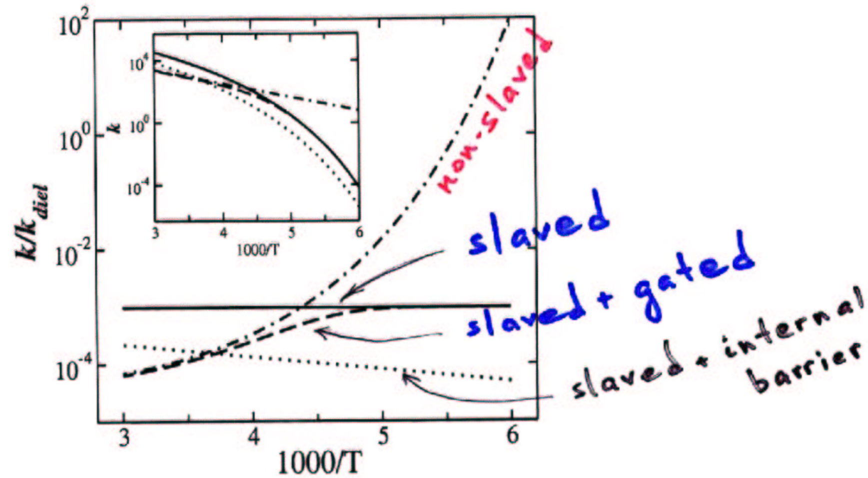


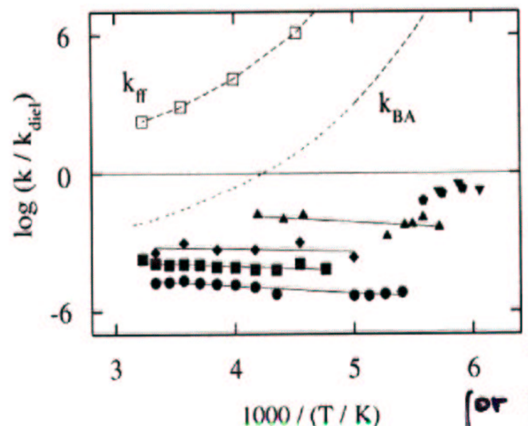
Diffusive Solvent Control



Gated Solvent Control

Alternative Kinetic Scenarios of Internal Processes in presence of Slaving





If slaved:

$$\frac{k}{k_{diel}} \sim \frac{1}{N_{st}}$$

N_{st} - # of distinct structural states nominally visited during relaxation (≫1), (or size of effective diffusion space)

Gives lower bound on native state entropy

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