Inherent Structures and Their Excitations
Jan. 2000 Author: Frank H. Stillinger

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Inherent Structures and their Excitations

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Areas of Application

- Lindemann melting law, freezing extension.
- Low-T two-level system identification.
- Vibration-free local order in liquids.
- Stress-strain ageing and rejuvenation phenomena.
- Mechanical strength of glasses.
- Structure of aerogels.
- Hole-burning dynamics.
- Nucleation events for freezing and cavitation.
- Anomalous density of crystalline **4**He.
- Capillary waves at liquid interfaces.
- Protein folding.
- Critique of "ideal glass transition."

Areas of Application (cont'd)

- T, p dependence of water structure.
- 2-dimensional melting and hexatic order.
- Liquid metals and alloys.
- Colloidal suspensions.
- Pressure-induced amorphization.
- Breakdown of Stokes-Einstein formula for self diffusion rate in s.-c. liquids.
- Thermally excited cluster rearrangements.
- Point defect formation pathways in solids.
- Formation of silica glass by dehydration reactions.
- Molten salts.
- Shock wave propagation.
- Fracture dynamics.

POTENTIAL ENERGY FUNCTIONS

- BORN-OPPENHEIMER GROUND ELECTRONIC STATE FOR N PARTICLES (MOLECULES, IONS, ATOMS):

$$\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N) .$$

- CHEMICAL INFORMATION:
  - MOLECULAR SIZE, SHAPE, FLEXIBILITY
  - MULTIPOLE MOMENTS, POLARIZABILITY
  - DISPERSION ATTRACTION
  - HYDROGEN BONDS
  - COVALENT BOND FORMATION, DISSOCIATION.

- MATHEMATICAL FORMAT AND PROPERTIES:

  Φ CONTINUOUS, DIFFERENTIABLE AWAY FROM NUCLEAR CONFLUENCES.

  $\Phi > -NB$ (STABILITY CRITERION).

- ADD pV TO Φ FOR CONSTANT PRESSURE CONDITIONS; CONFIGURATION SPACE DIMENSION:

$$(3+\nu)N \qquad (\text{CONST. } V),$$

$$(3+\nu)N+1 \qquad (\text{CONST. } p),$$

ν = NUMBER OF INTERNAL DEGREES OF FREEDOM PER PARTICLE.

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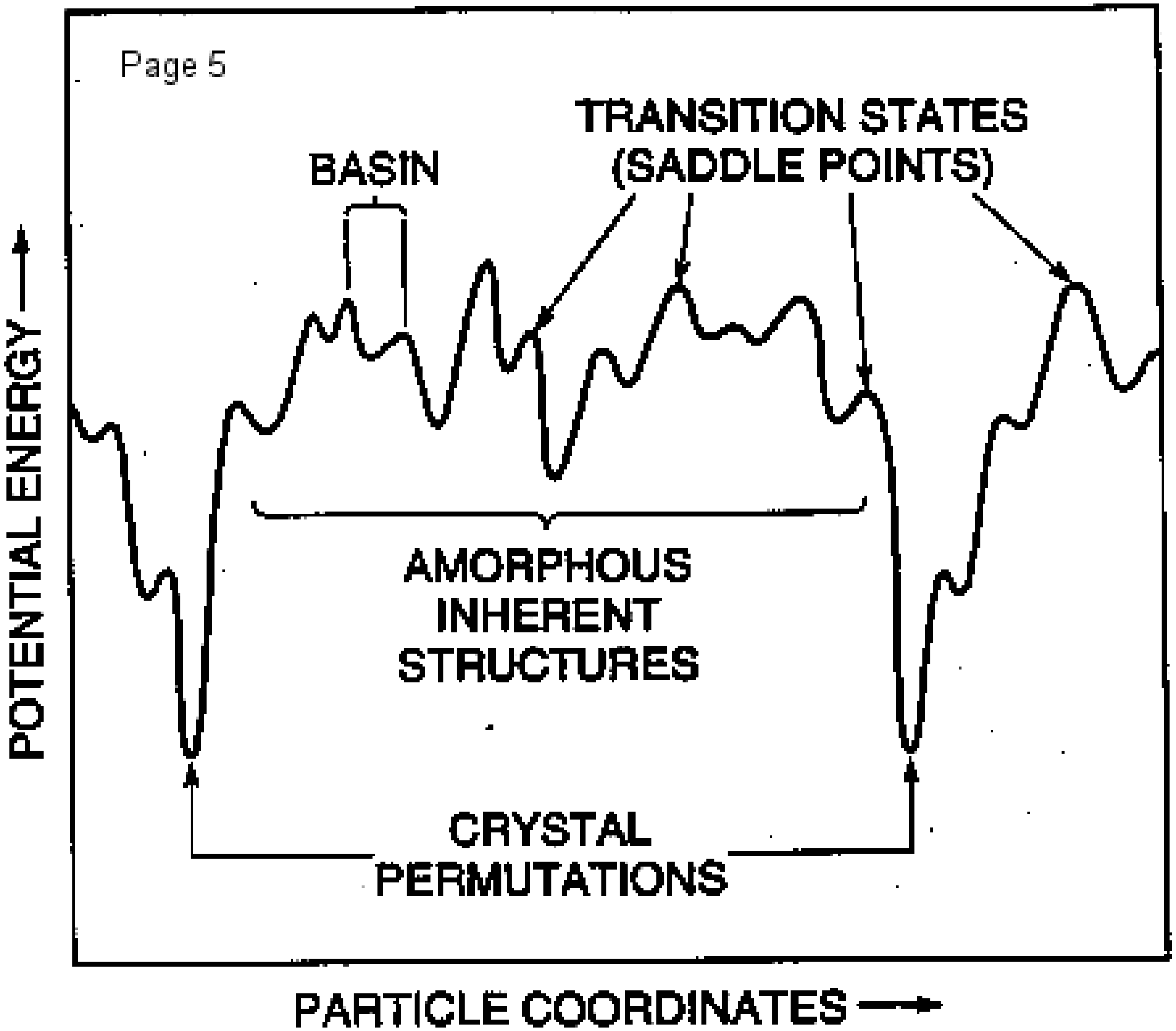

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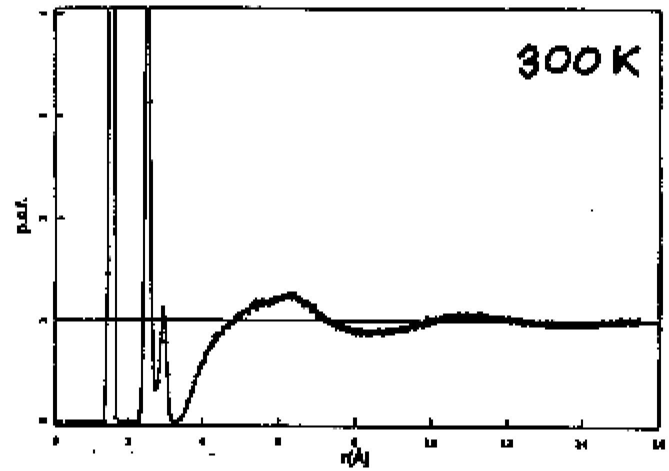
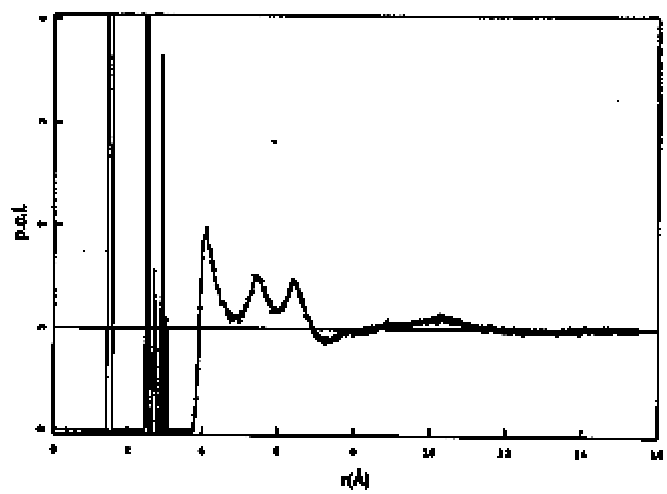
BASIN PROPERTIES

- DEFINED BY STEEPEST DESCENT ON Φ HYPERSURFACE.
- NUMBER OF BASINS $\sim N! \exp(\alpha N)$, $\alpha > 0$.
- SPAN OF Φ MINIMA $= O(N)$.
- ELEMENTARY INTERBASIN TRANSITIONS ARE:
  - (a) LOCALIZED [SHIFT OF $O(1)$ PARTICLES],
  - (b) SELDOM PURELY PERMUTATIONAL.
- $O(N)$ TRANSITION STATES (SIMPLE SADDLE POINTS) IN EACH BASIN BOUNDARY.
- INTERBASIN TRANSITION RATE FOR POSITIVE TEMPERATURE IS $O(N)$.
- TRANSITION STATE BARRIERS CAN BE ARBITRARILY SMALL IN THE "AMORPHOUS" REGION OF CONFIGURATION SPACE (QUANTIZED 2-LEVEL SYSTEMS IN LOW TEMPERATURE GLASSES).
- BASINS NEED NOT BE SIMPLY CONNECTED.
- BASINS MAY CONTAIN INTERIOR SADDLE POINTS.

CYCLOHEXANE, C–C PAIRS



S. D. QUENCH



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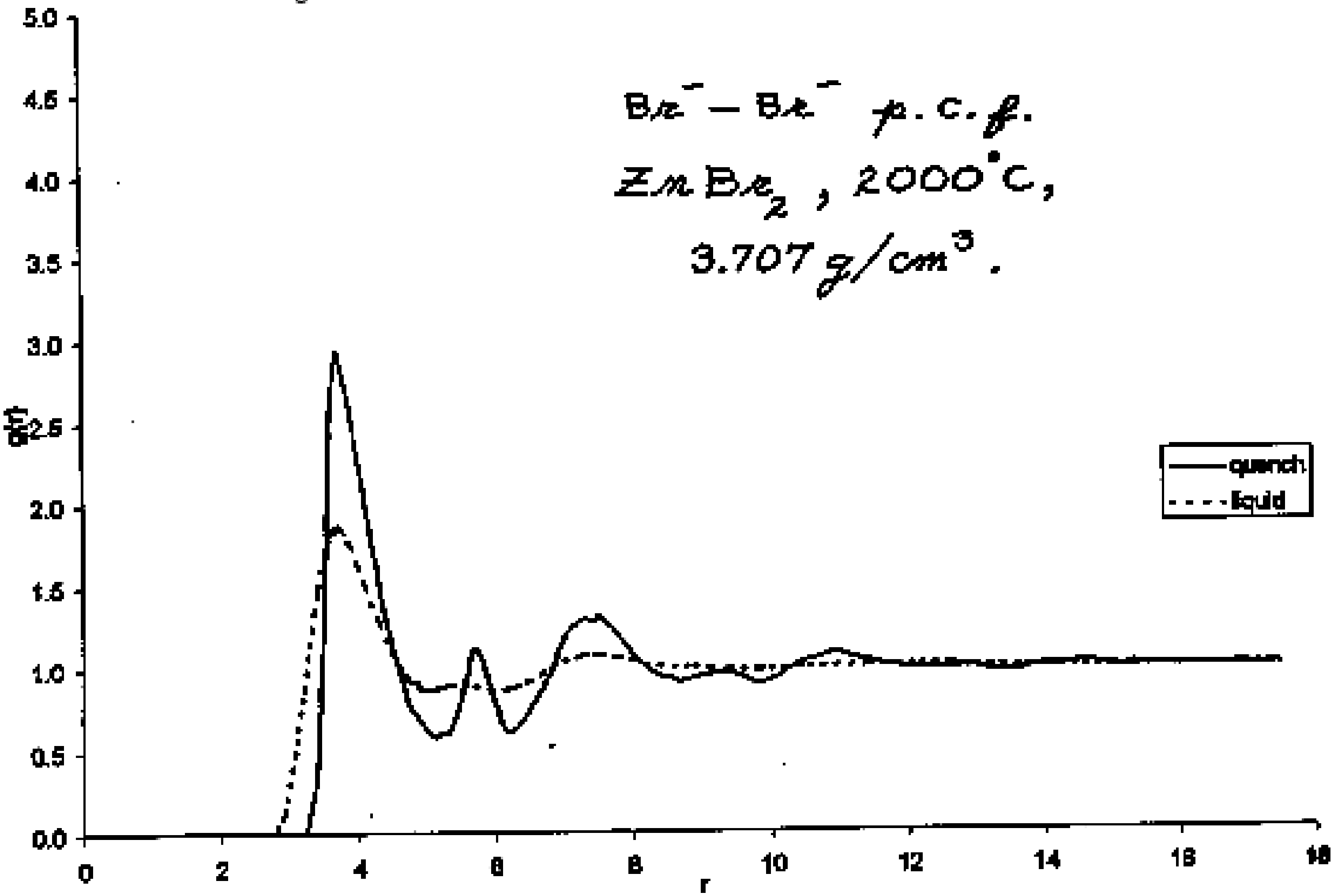

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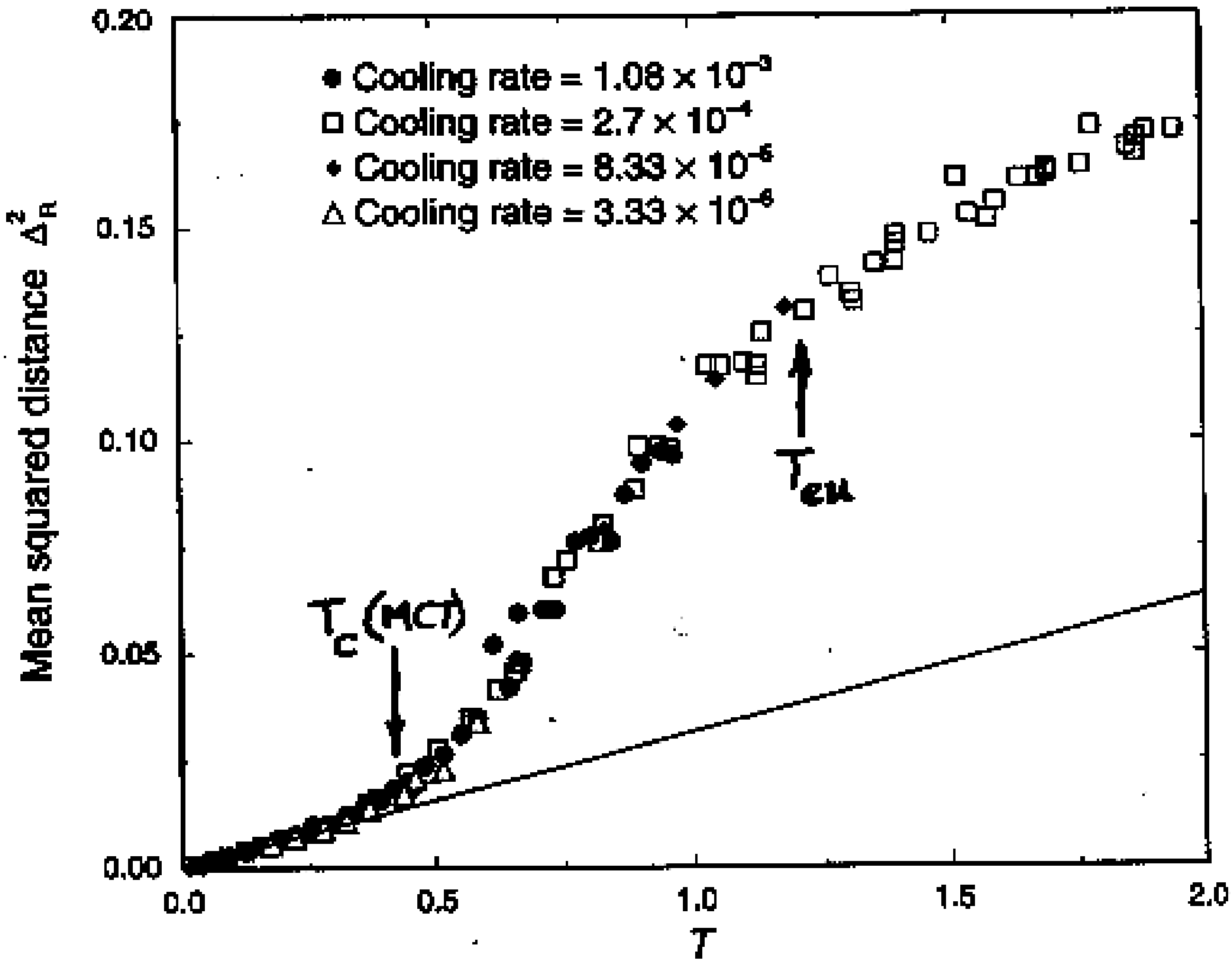
"$Ni_{80}P_{20}$"



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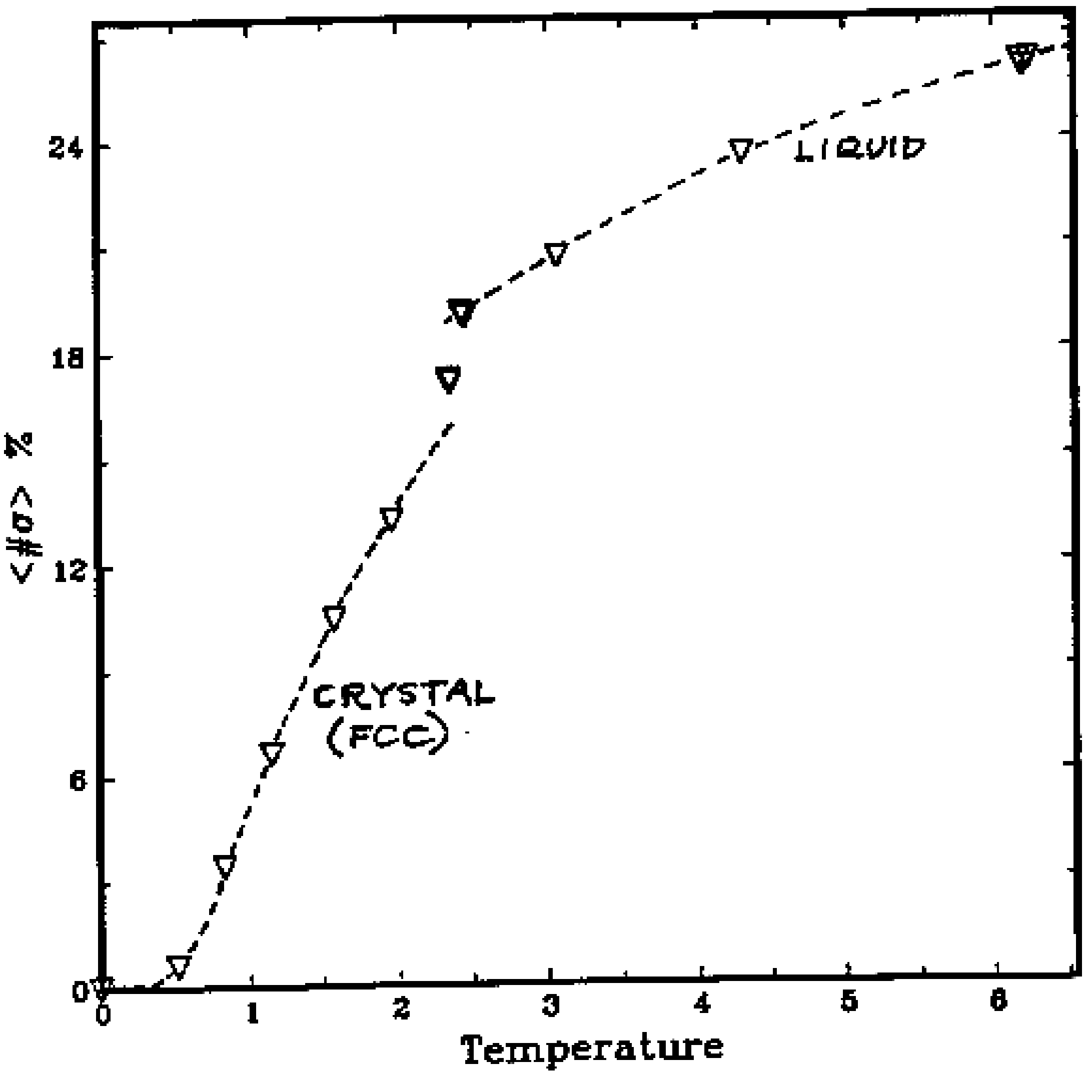
PERCENTAGE OF HESSIAN EIGENVALUES THAT ARE NEGATIVE



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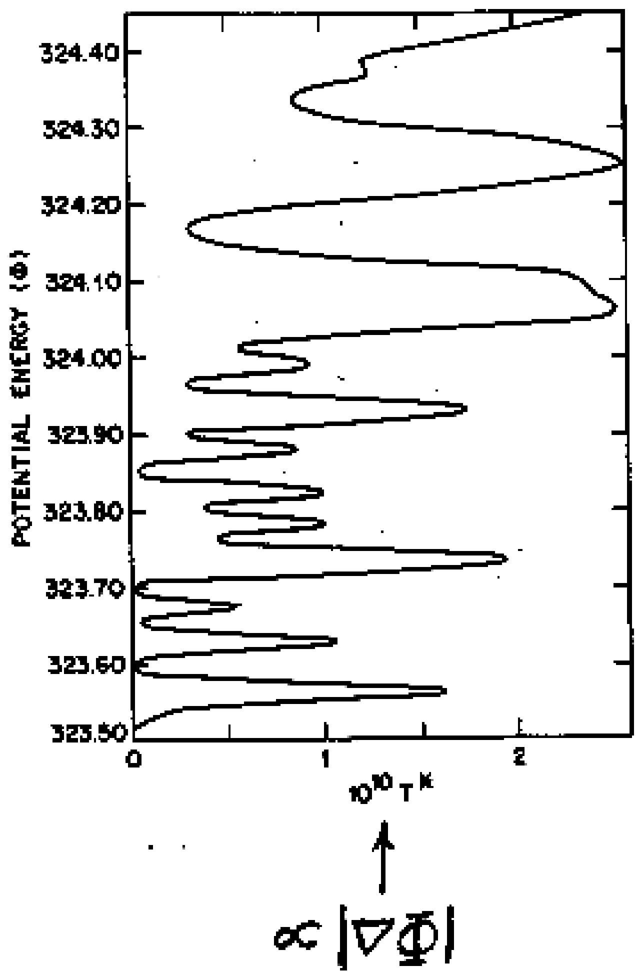
2-D GCM



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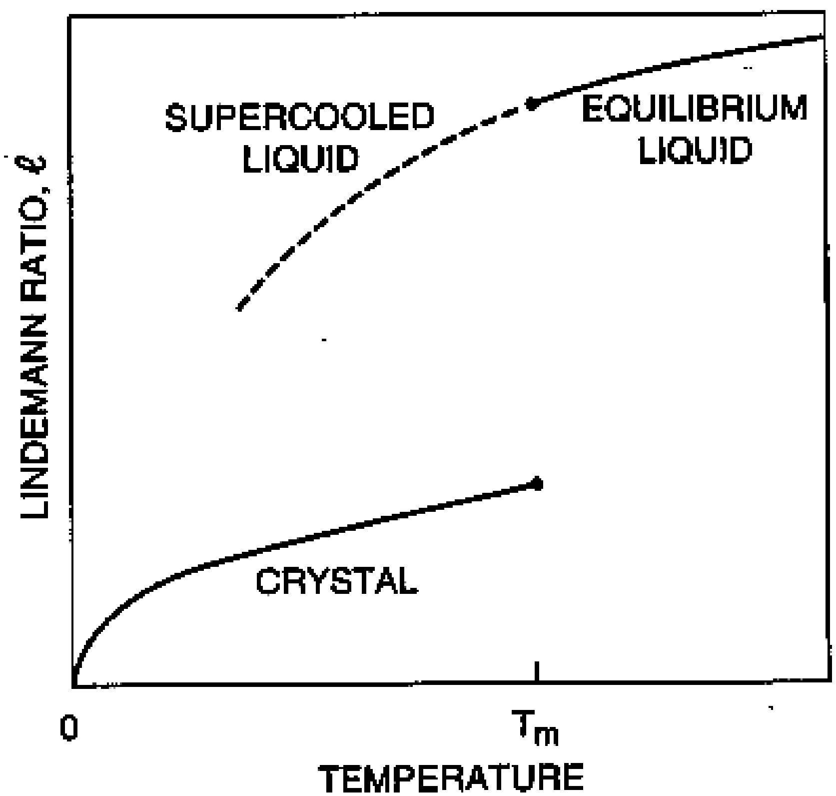
LINDEMANN MELTING CRITERION:

$$\ell = \langle (\Delta \mathbf{r}_i)^2 \rangle / a$$

$$\cong 0.15 \text{ AT } T_m .$$



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INHERENT STRUCTURE REPRESENTATION

- ENUMERATE POTENTIAL MINIMA (INHERENT STRUCTURES) BY DEPTH PER PARTICLE $\Phi/N \equiv \varphi$:

$$\text{DENSITY} = N!\,\exp[N\sigma(\varphi)] \,.$$

- MEAN VIBRATIONAL FREE ENERGY PER PARTICLE FOR DEPTH φ:

$$\exp[-N f_v(\beta,\varphi)] = \Big\langle \int_{\underset{\text{BASIN}}{B_\alpha}} d^{3N}\underset{\sim}{R}\, \exp[-\underset{(k_B T)^{-1}}{\beta}\, \Delta_\alpha \Phi(\underset{\sim}{R})] \Big\rangle_\varphi \,.$$

- EXACT FREE ENERGY:

$$\beta F/N = \ln \underset{\substack{\text{THERMAL}\\ \text{WAVELENGTH}}}{\lambda_T^3} \underbrace{-\sigma(\varphi^*) + \beta\varphi^* + \beta f_v(\beta,\varphi^*)}_{\text{MINIMIZED BY } \varphi^*(\beta)} \,.$$

- PRESSURE: $$p = -\left(\frac{\partial F/N}{\partial V/N}\right)_\beta$$

$$\geq 0 \quad \text{AT EQUILIBRIUM} \,.$$

- $\varphi^*(\beta)$ SINGULAR AT PHASE TRANSITIONS.

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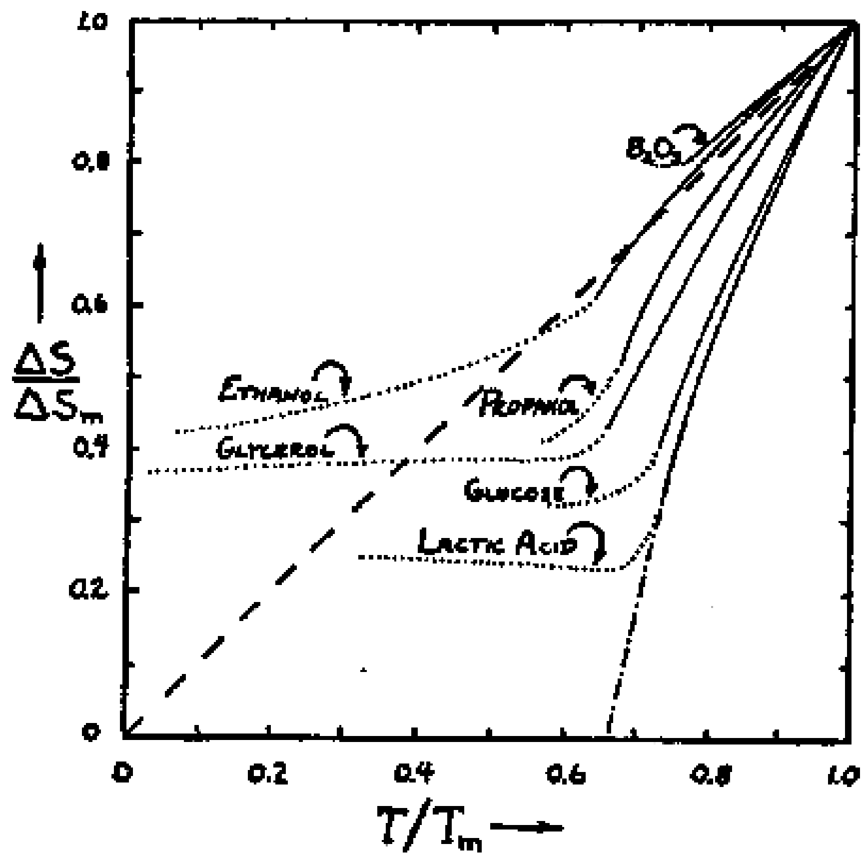
W. KAUZMANN, CHEM. REVS. 43, 219 (1948)



IDEAL GLASS TRANSITION?

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Inherent Structure Implications for the "Kauzmann Paradox"

• Ideal glass transition at T>0 is not possible: It would require infinite structural excitation energy out of lowest glass basin.

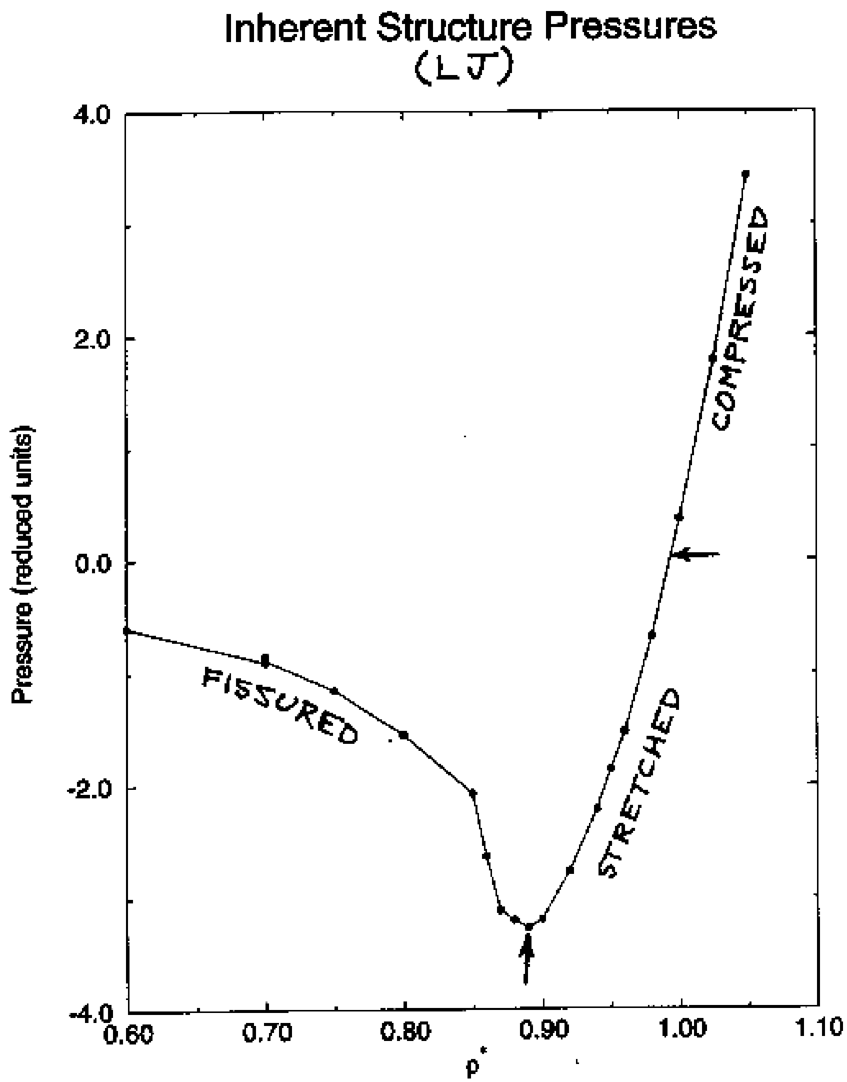
• It is possible to have

$$S_{liq} - S_{crys} < 0$$

if and only if

$$S_{liq}^{(vib)} - S_{crys}^{(vib)} < 0$$

is sufficiently large in magnitude and negative.



$p_{min}/p_c \cong -30$

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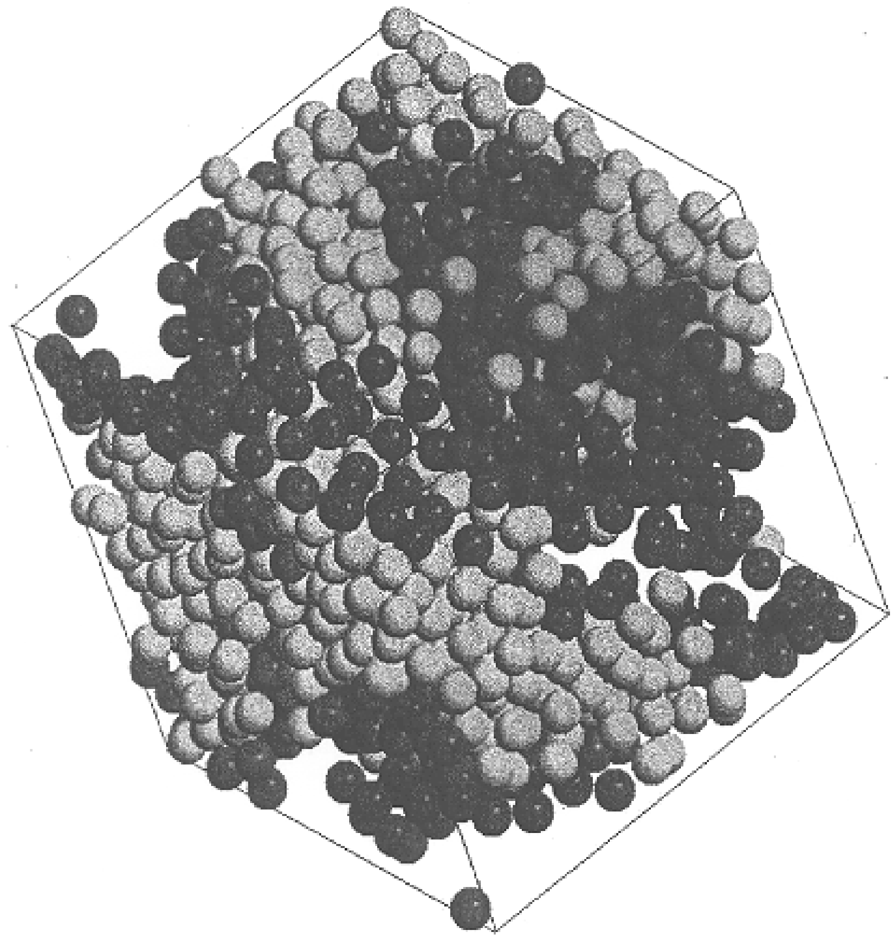

$N = 1372$

$\rho^* = 0.725\ , \quad T^*_{initial} = 0.9$

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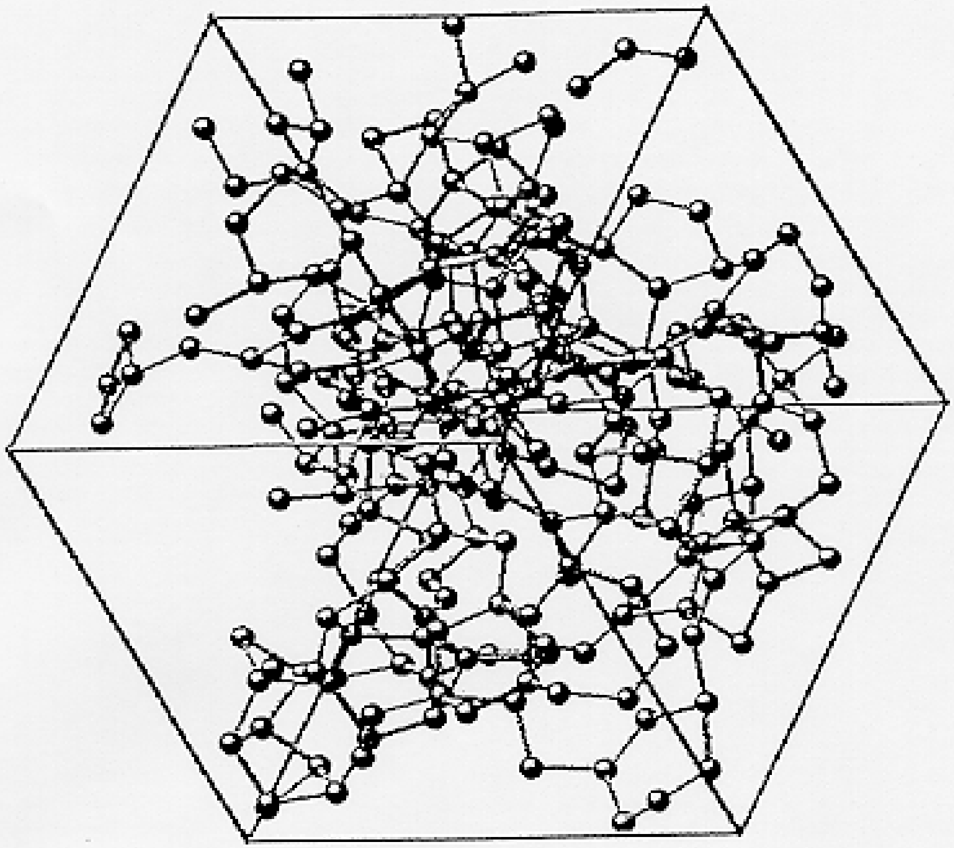
SPC/E "WATER",

0.6 G/CM^3



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Low-Density Regime

- Enumeration of inherent structures:

$$\Omega\,(N,V) \approx N!\,\exp[\,\alpha\,(N/V)N]\ \ (\,\alpha\mathbf{>0})$$

- Consequence of attractions:

  (1) Spatially inhomogeneous structures;

  (2) $\lim\limits_{N/V \to 0} \alpha\,(N/V) = +\infty$.

- Large finite N, infinite V:

  (1) Fractal structures (cf. "DLA");

  (2) $\Omega(\,N\,,\infty) \approx N!\,\exp[KN \cdot \ln N + O(N)]$

  $\approx (N!)^{\mathbf{1+K}} \qquad (K>0)$.

- Connection with aerogels.

Challenging Problem

• Born-Green-Yvon equation:

$$-k_B T \nabla_1 \ln g^{(2)}(r_{12}) = \nabla_1 V(r_{12}) + \rho \int d\mathbf{r}_3 [\nabla_1 V(r_{13})] \times g^{(2)}(r_{13}) g^{(2)}(r_{23}) K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3).$$

• Kirkwood superposition defect:

$$K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{g^{(3)}(r_1, r_2, r_3)}{g^{(2)}(r_{12}) g^{(2)}(r_{13}) g^{(2)}(r_{23})}$$

• T $\rightarrow 0$ for inherent structures:

$$0 = \nabla_1 V(r_{12}) + \rho \int d\mathbf{r}_3 [\nabla_1 V(r_{13})] K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \,|\, T=0) \times g_q^{(2)}(r_{13}) g_q^{(2)}(r_{23}).$$

• Questions:

(1) $g_q^{(2)}$ uniquely determined by K?

(2) How does K depend on method of preparing T = 0 deposit?