Liquids and Glasses under Tension

Slides for a lecture for a class in the Dept. of Chemistry, Princeton University
CHE 552 lecture, Tuesday, November 27,2001

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Liquids and Glasses Under Tension

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Outline

- Negative pressure (isotropic tension) experiments.

- Implications of the van der Waals equation of state.

- Virial equation of state: Role of interactions and short-range order.

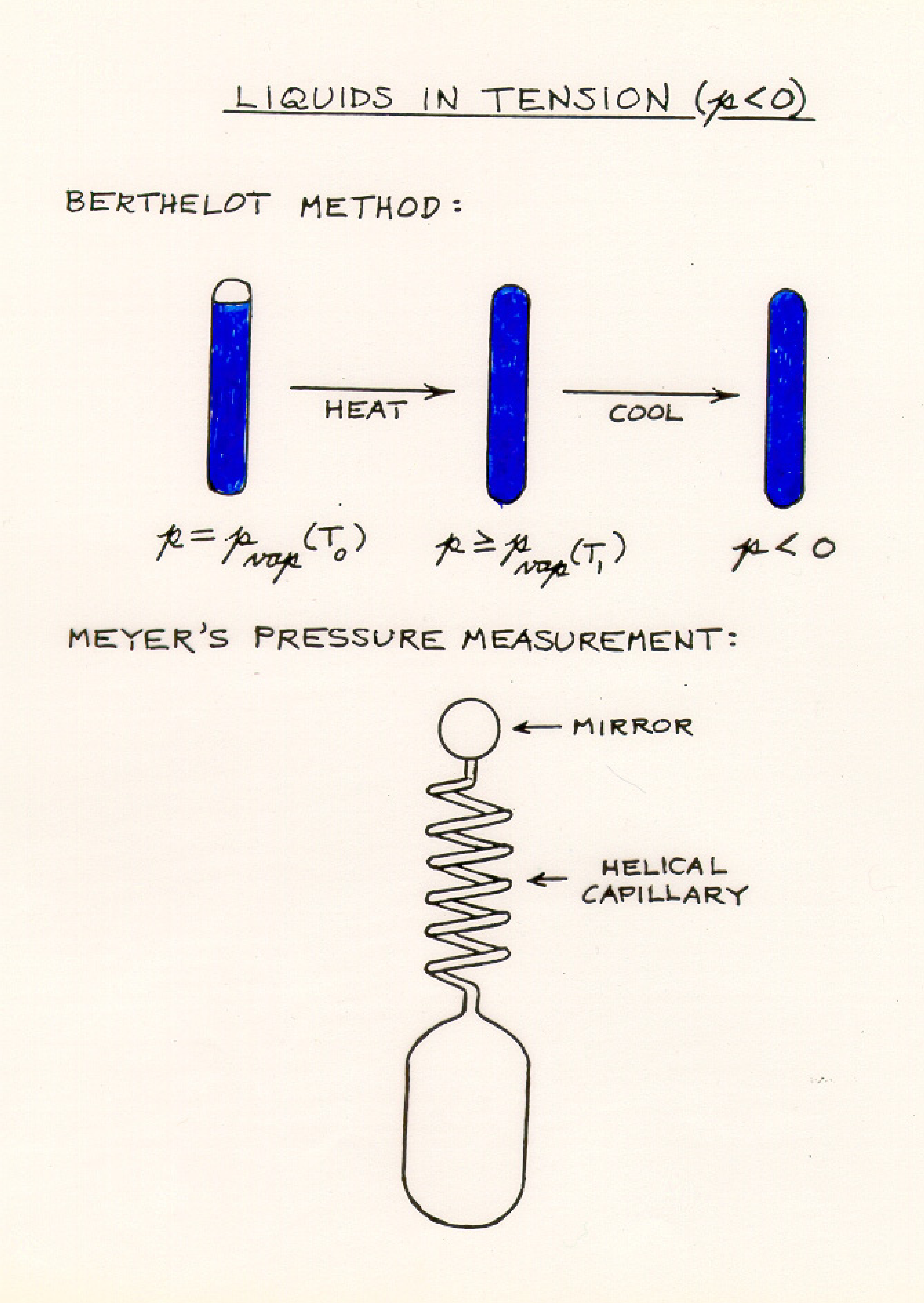
- Connections to the "inherent structure" representation of liquids and glasses.

- Some results from computer simulations for various substances: Shredding (Sastry) density and maximal strength.

- Kauzmann curves and their apparent connection to the T + 0 limiting liquid spinodal.

- Relevant research topics.

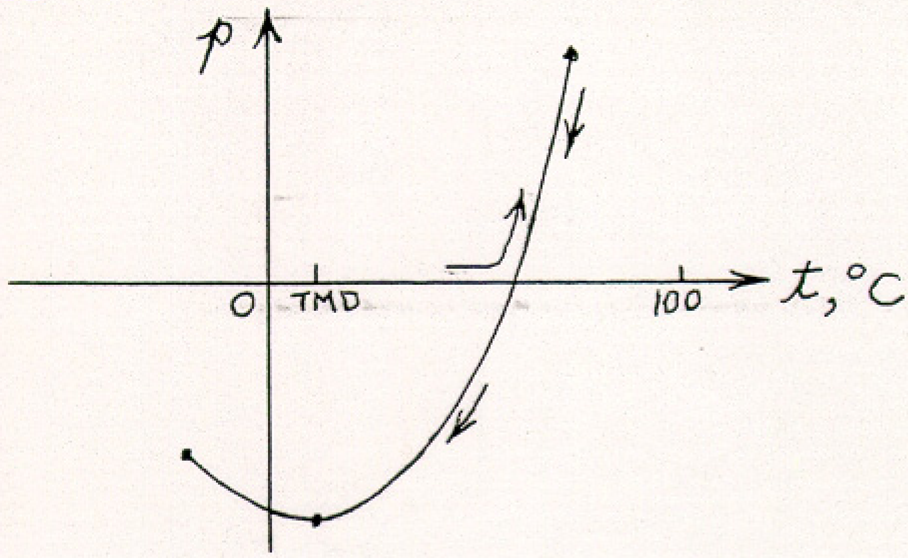
Berthelot and Meyer experimental methods



Negative-pressure measurements for water

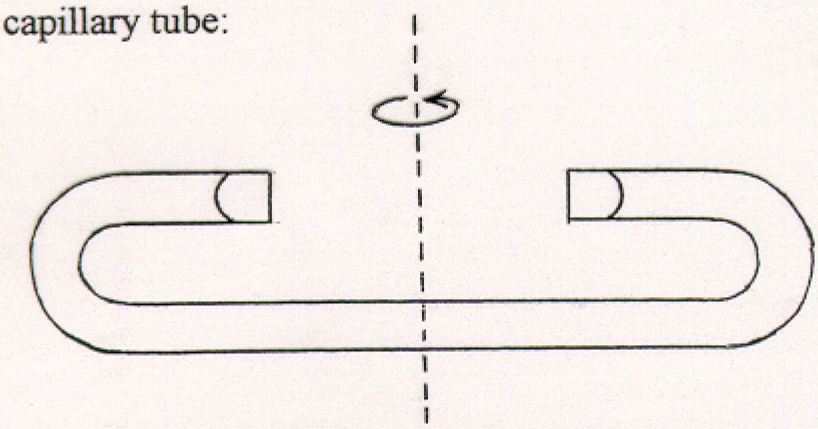
Negative-Pressure Measurements for Water

- The Berthelot/Meyer technique is frustrated by water's negative thermal expansion. Typical result locates point on line of density maxima:



Maximum tension observed: ≅ −230 bar.

- Alternative method utilizes centrifugal force in a rapidly spinning bent capillary tube:



References: L.J. Briggs, J. Appl. Phys. **21**, 721 (1950);
J. Winnick and S.J. Cho, J. Chem. Phys. **55**, 2092 (1971).
Maximum tension observed: −277 bar.

- Microscopic aqueous inclusions in quartz crystals imply maximum tension of −1400 bar at 42° C. Reference: Q. Zheng, D.J. Durben, G.H. Wolf, and C.A. Angell, Science **254**, 829 (1991).

van der Waals Equation of State

- Conventional form:

$$p = \frac{Nk_B T}{V - Nb} - \frac{N^2 a}{V^2} \quad .$$

The "physical" region is $V \geq Nb$.

- Critical-point values:

$$p_c = \frac{a}{27b^2} \quad , \quad k_B T_c = \frac{8a}{27b} \quad , \quad v_c \equiv \frac{V_c}{N} = 3b \quad ,$$

$$\frac{p_c v_c}{k_B T_c} = \frac{3}{8} \quad .$$

- Reduced form ($p^* = p / p_c$, etc.):

$$p^* = \frac{8T^*}{3v^* - 1} - \frac{3}{v^{*2}} \quad .$$

- Spinodal curves $v^*_{sp}(T^*)$ determined by cubic polynomial:

$$v^{*3} - (3v^* - 1)^2 / (4T^*) = 0 \quad .$$

- Liquid spinodal becomes negative for $T^* < 27/32 = 0.84375$.

Mayer & Mayer reduced plot; $p_{min}(T=0) = -27p_c$

J.E. Mayer and M.G. Mayer, *Statistical Mechanics* (Wiley, 1940):

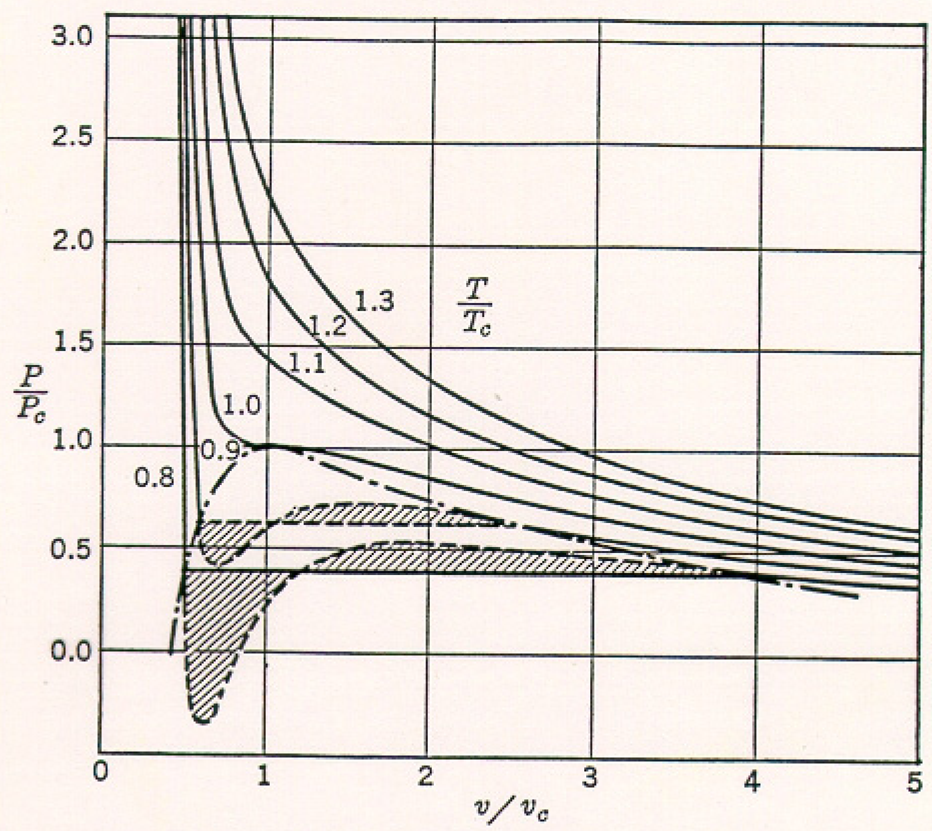


FIG. 12. 2. van der Waal's equation. Plot of P/P_c against v/v_c for various values of T/T_c. $\frac{P}{P_c} = \frac{8(T/T_c)}{3(v/v_c) - 1} - \frac{3}{(v/v_c)^2}$.

Minimum of T=0 isotherm (maximum sustainable tension):

$$p_{\min}(T=0) = -27 p_c$$

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Virial Equation of State

- N-body system with pairwise-additive, spherically symmetric interactions:
$$\Phi(\mathbf{r}_1 \ldots \mathbf{r}_2) = \sum_{i<j} v(r_{ij}) \quad .$$

- Virial equation for pressure in a thermal equilibrium state:
$$p = \rho k_B T - (2\pi\rho^3/3)\int_0^\infty r^3 v'(r) g^{(2)}(r,\rho,T)dr \quad ;$$
$$\rho = N/V \quad , \quad g^{(2)} = \text{pair correlation function} \quad .$$

- Virial expansion (virial coefficients) generated by inserting:
$$g^{(2)}(r,\rho,T) = \exp[-v(r)/k_B T][1 + \sum_{n=1}^{\infty} \rho^n \gamma_n(r,T)] \quad .$$

- Application to metastable states (supercooled liquid, overcompressed vapor, superheated crystal, ...) requires an appropriate $g^{(2)}(r,\rho,T)$. In theory this requires evaluating $g^{(2)}$ only for a restricted portion of the full N-body configuration space that is relevant to the metastable phase.

- The virial expression above for pressure can be generalized to:
  (a) nonspherical and flexible molecules,
  (b) nonadditive (many-body) interactions,
  (c) mixtures of different species.

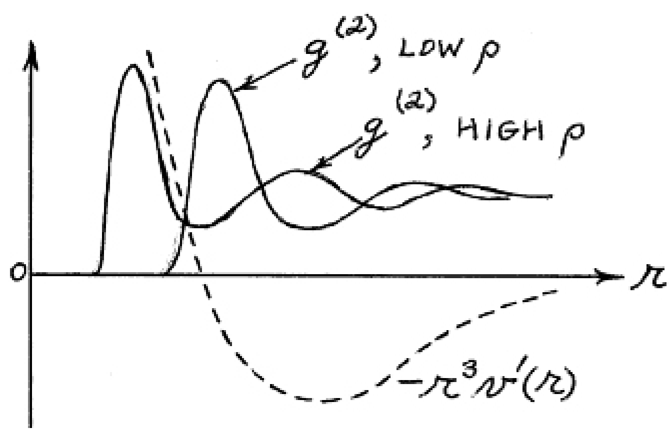
Virial Equation of State – Competing Contributions

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

- Liquid Argon at its triple point has:
  $\rho = 0.02130 A^{-3}$, $T = 84K$,
  which imply the following ideal gas pressure:
  $p_{ideal} = \rho k_B T = 247 bar$.

- However, the measured triple-point pressure for Argon is $0.6 bar$. Consequently the ideal-gas, and interaction contributions to the virial pressure nearly cancel one another.

- Integrand factors:



- Approach to liquid spinodal at $T > 0 \Rightarrow$ large density fluctuations $\Rightarrow$ long-range deviations of $g^{(2)}(r)$ above unity ("critical" fluctuations). However the limit $T \to 0$ suppresses this effect.

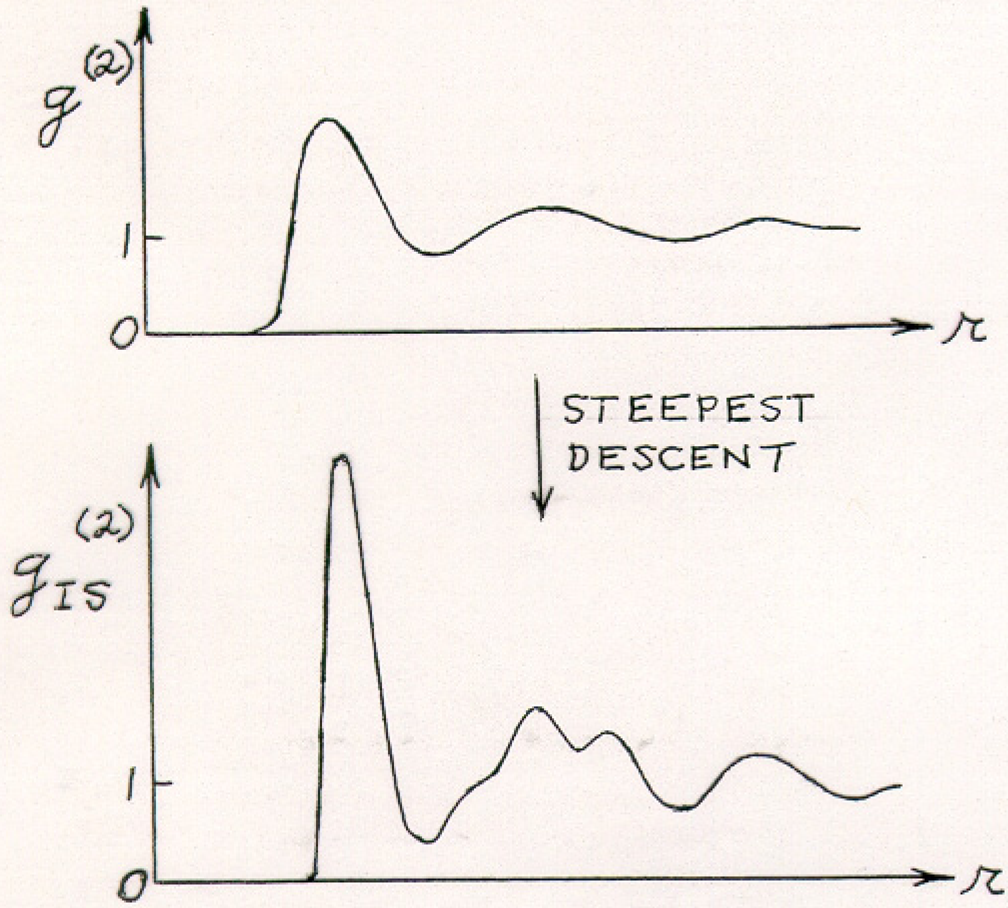
- p_{ideal} becomes small as the number of atoms/molecule increases, and vanishes in the high polymer limit.

Effects (on $g^{(2)}$,p) of mapping to inherent structures

Effects of Mapping to Inherent Structures

- Steepest-descent paths on N-body potential energy surface connect arbitrary particle configurations to their "parent" force-free inherent structures (potential minima).

- Removal of intrabasin vibrational displacements by steepest-descent mapping to minima sharpens image of short-range order for any phase. Qualitative result for liquids:



- Pre-mapping virial equation for pressure:

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

- Post-mapping version:

$$p(inh.str.) = -(2\pi\rho^2 / 3)\int_0^\infty r^3 v'(r) g_{IS}^{(2)}(r,\rho)dr \ .$$

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Inherent Structure "T=0 Isotherms"

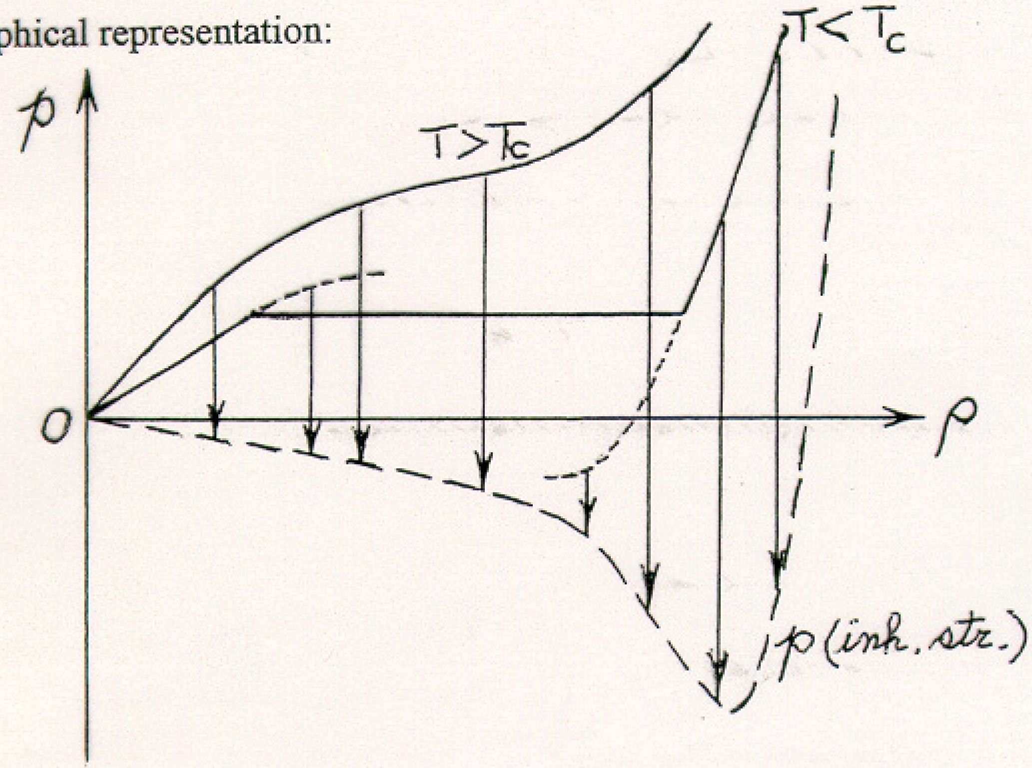
- Steepest-descent mapping on the N-body potential energy surface Φ relates any initial particle configuration to its parent inherent structure.

$$d\mathbf{r}_i(s)/ds = -\nabla_{\mathbf{r}_i}\Phi(\mathbf{r}_1 \dots \mathbf{r}_N) \qquad (0 \le s < \infty) \ .$$

- Carry out mapping of representative sample of fluid-state configurations. Calculate virial pressure for corresponding collection of inherent structures. Owing to removal of "intrabasin" vibrational motions,

$$p(inh.strs.) < p(fluid) \ .$$

- Graphical representation:



- Pressure curve for inherent structures is substantially independent of pre-mapping T for "simple" liquids, slightly T-dependent for "complex" liquids.

- $p(inh.str.)$ may be interpreted as the $T=0$ limit of the supercooled liquid isotherm. Therefore its minimum corresponds to the $T=0$ limit of the liquid spinodal curve.

ILLUSTRATIVE MODEL: 1D L-J SYSTEM

- N PARTICLES, SYSTEM LENGTH L, PERIO[D]
  BOUNDARY CONDITIONS.

- POTENTIAL ENERGY FUNCTION:

$$\Phi(1\ldots N) = \sum_{\mu=-\infty}^{+\infty} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v(x_i - x_j + \mu L),$$

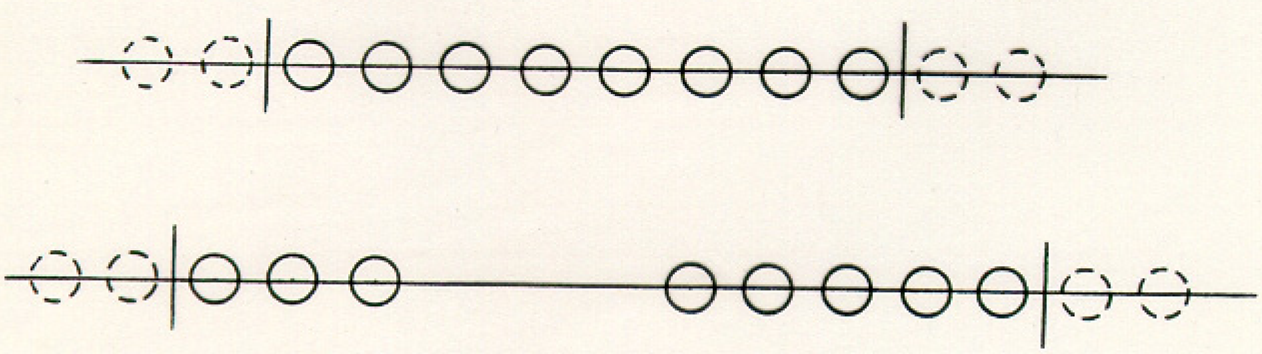
$$v(y) = 4(y^{-12} - y^{-6}).$$

- INHERENT STRUCTURES:

  A. $0 < L/N \leq \ell_0 \cong 1.1193 \Rightarrow$ PERIODIC CHAIN.

  B. $\ell_0 < L/N \leq \ell_1 \cong 1.2409 \Rightarrow$ PERIODIC CHAIN, SINGLY BROKEN C

  C. $\ell_1 < L/N \Rightarrow$ SINGLY BROKEN CHAIN.



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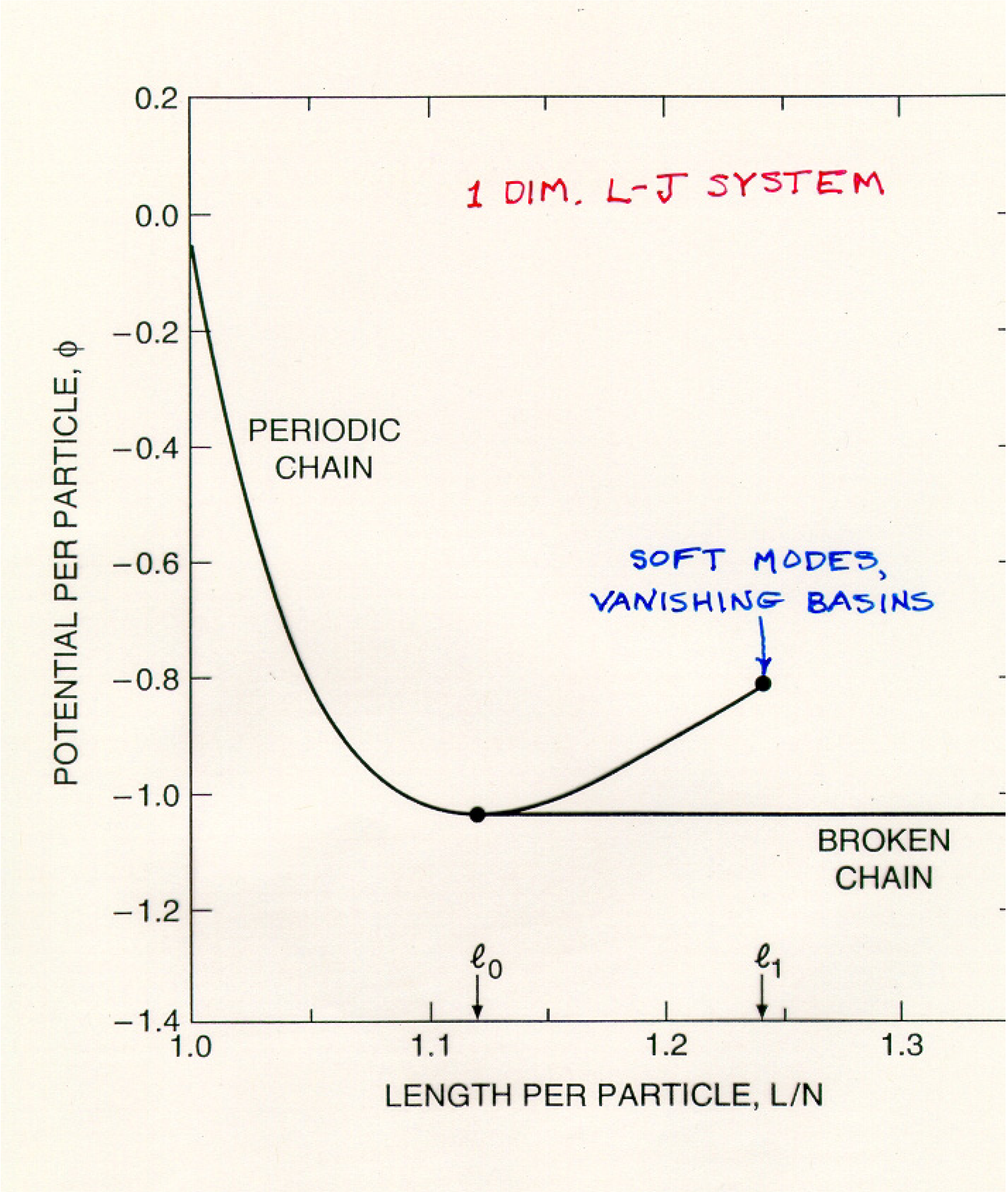
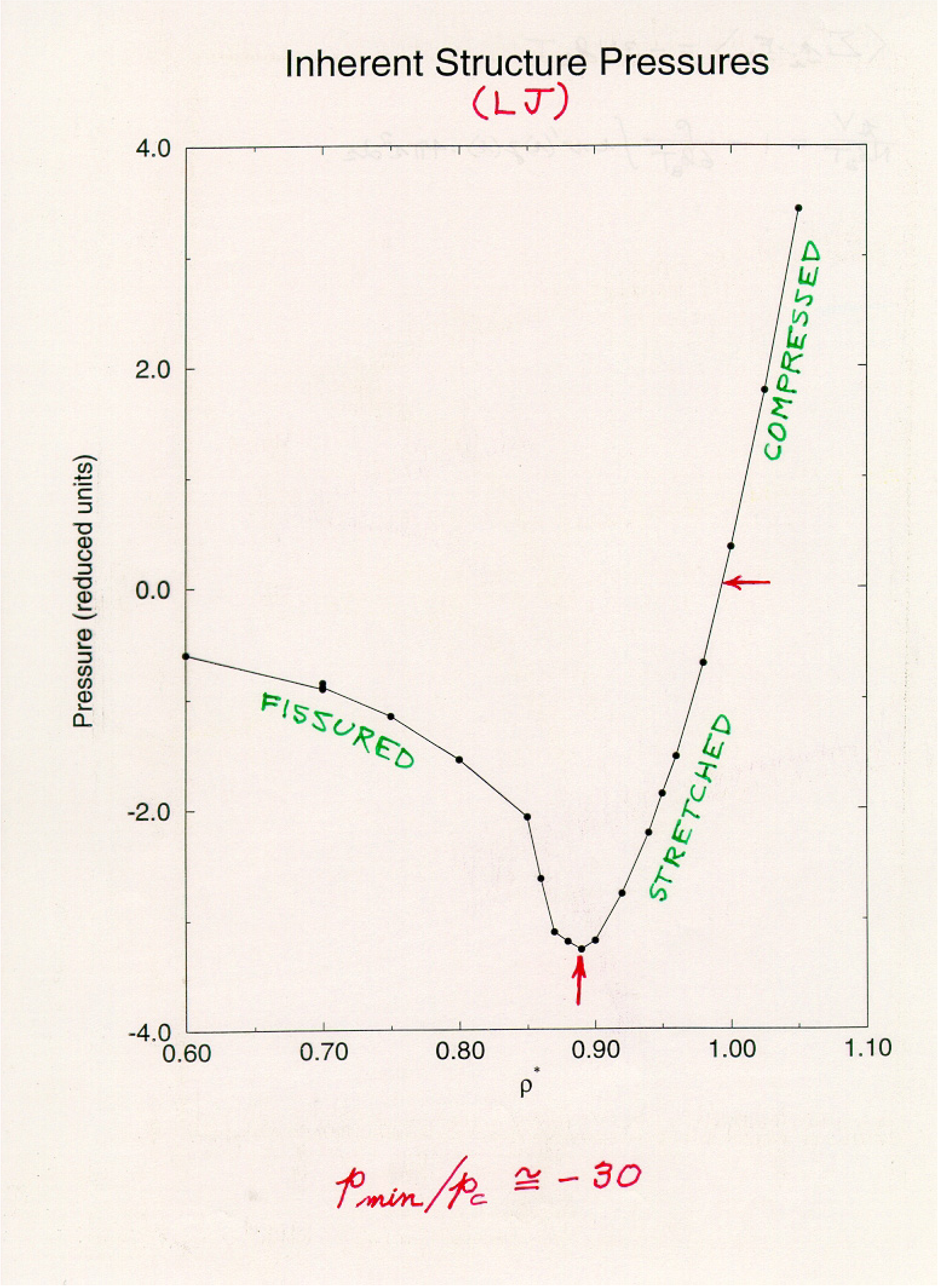
Inherent structure energies vs. L/N, 1D L-J system



p(inh. str.) for 3D L-J system; $p_{min}/p_c = -30$



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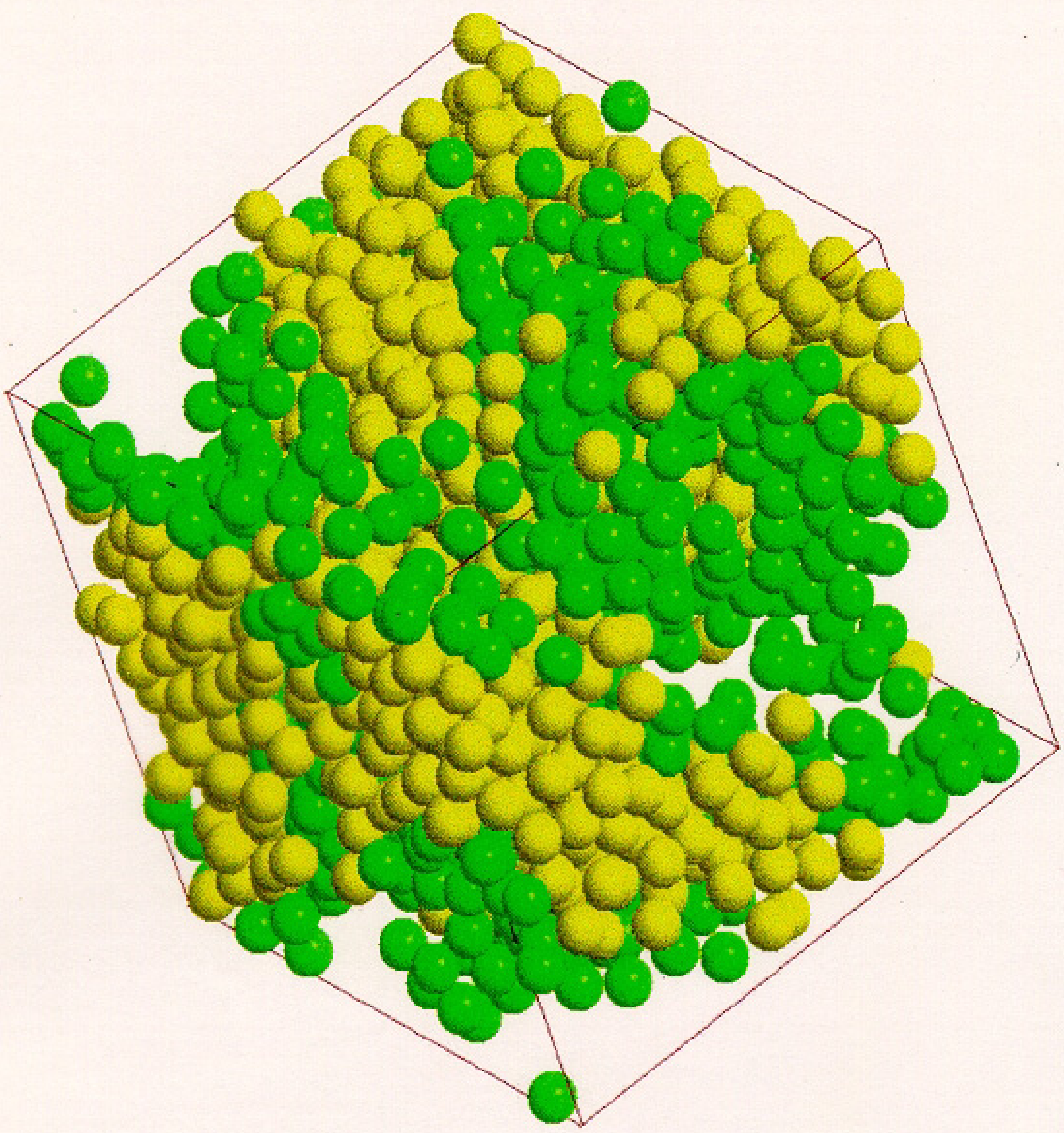
Fissured L-J configuration, N=1372



$N = 1372$

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

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Two SPC/E water p(inh. str.) curves

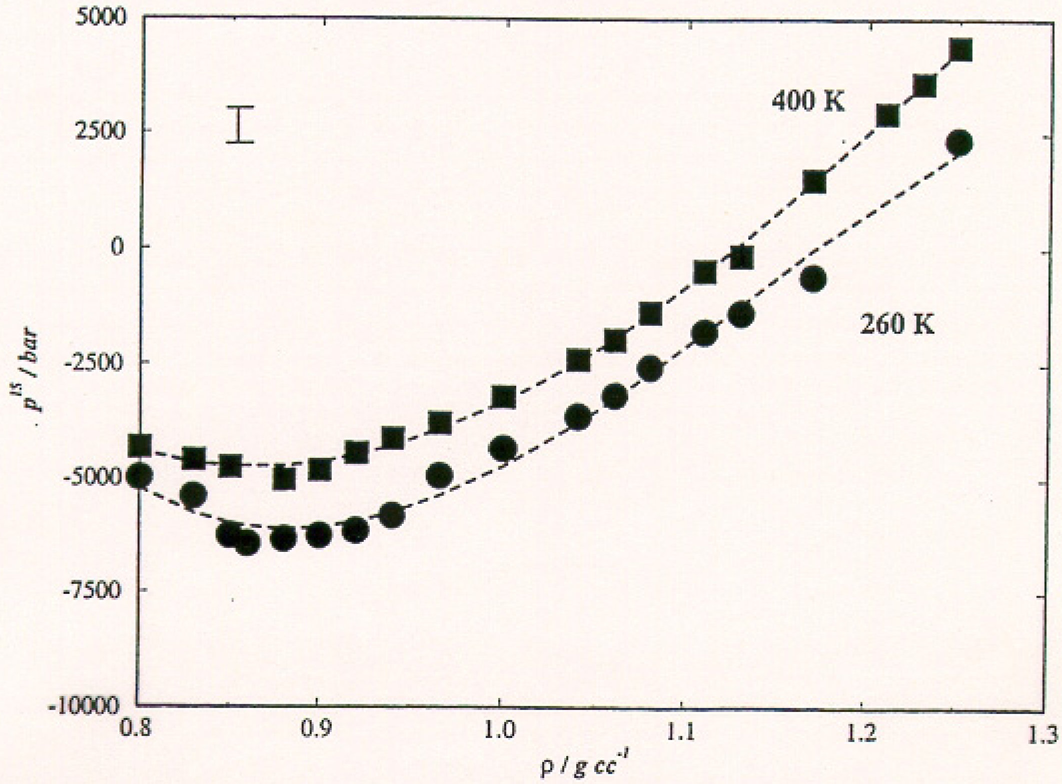
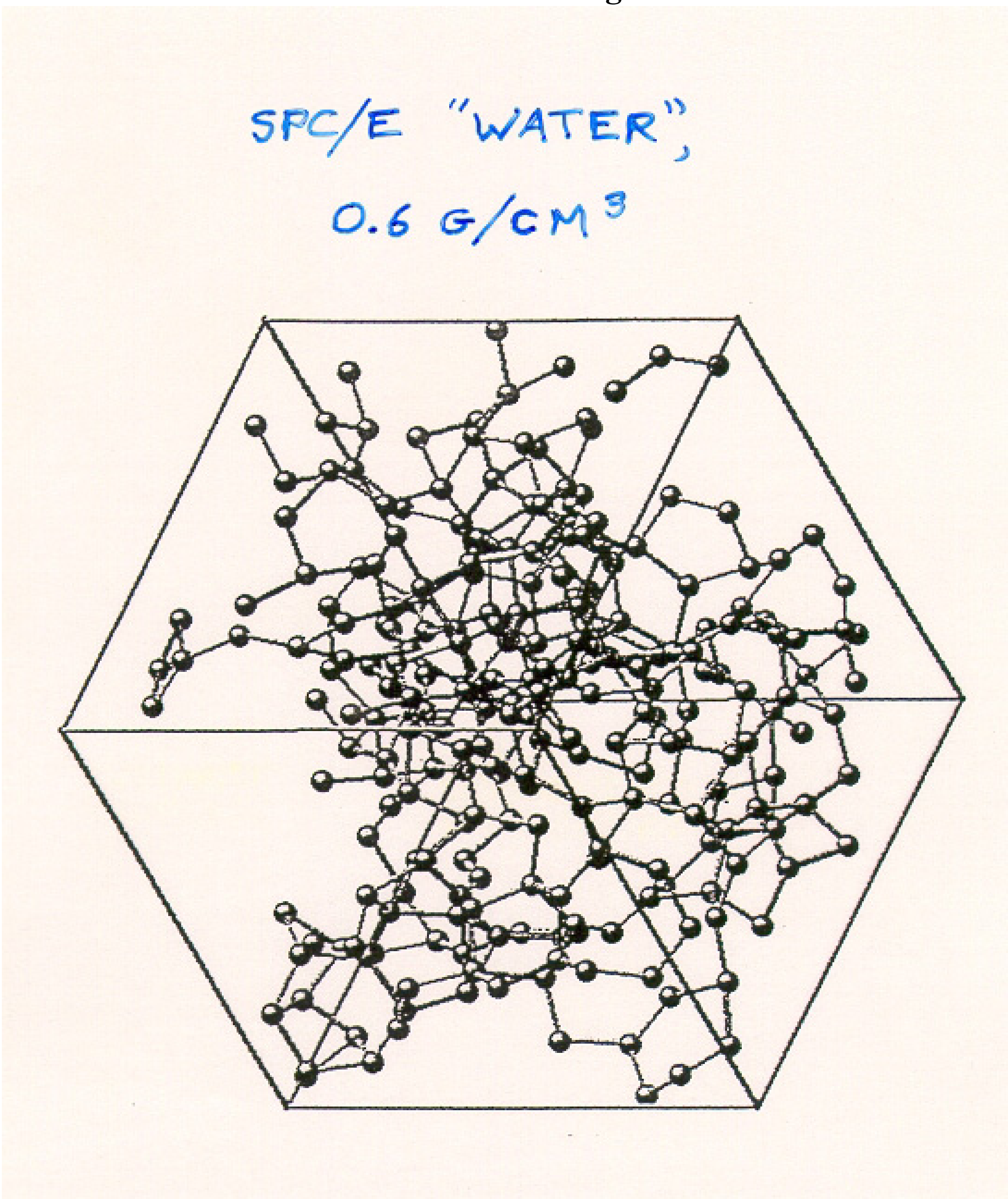
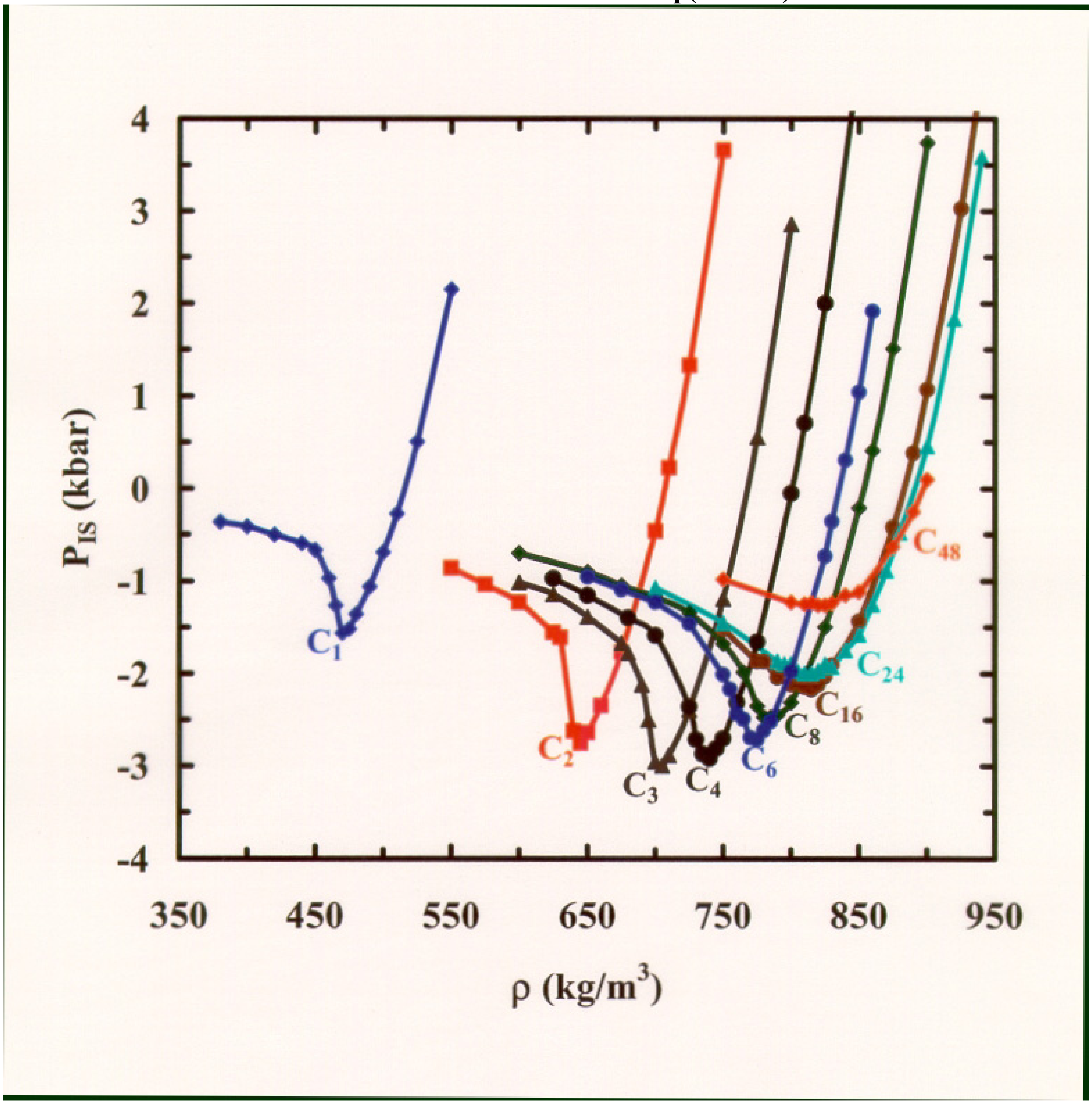


Figure 3. The equation of state of the energy landscape for the SPC/E potential: inherent structure pressure as a function of density $p^{IS}(\rho)$ along isotherms of 260 K (circles) and 400 K (squares). The temperatures are those of the equlibrated liquid from which the inherent structures were obtained. A typical error bar is included in the upper left corner.

Fissured SPC/E configuration



Vincent Shen's alkane results for p(inh. str.)



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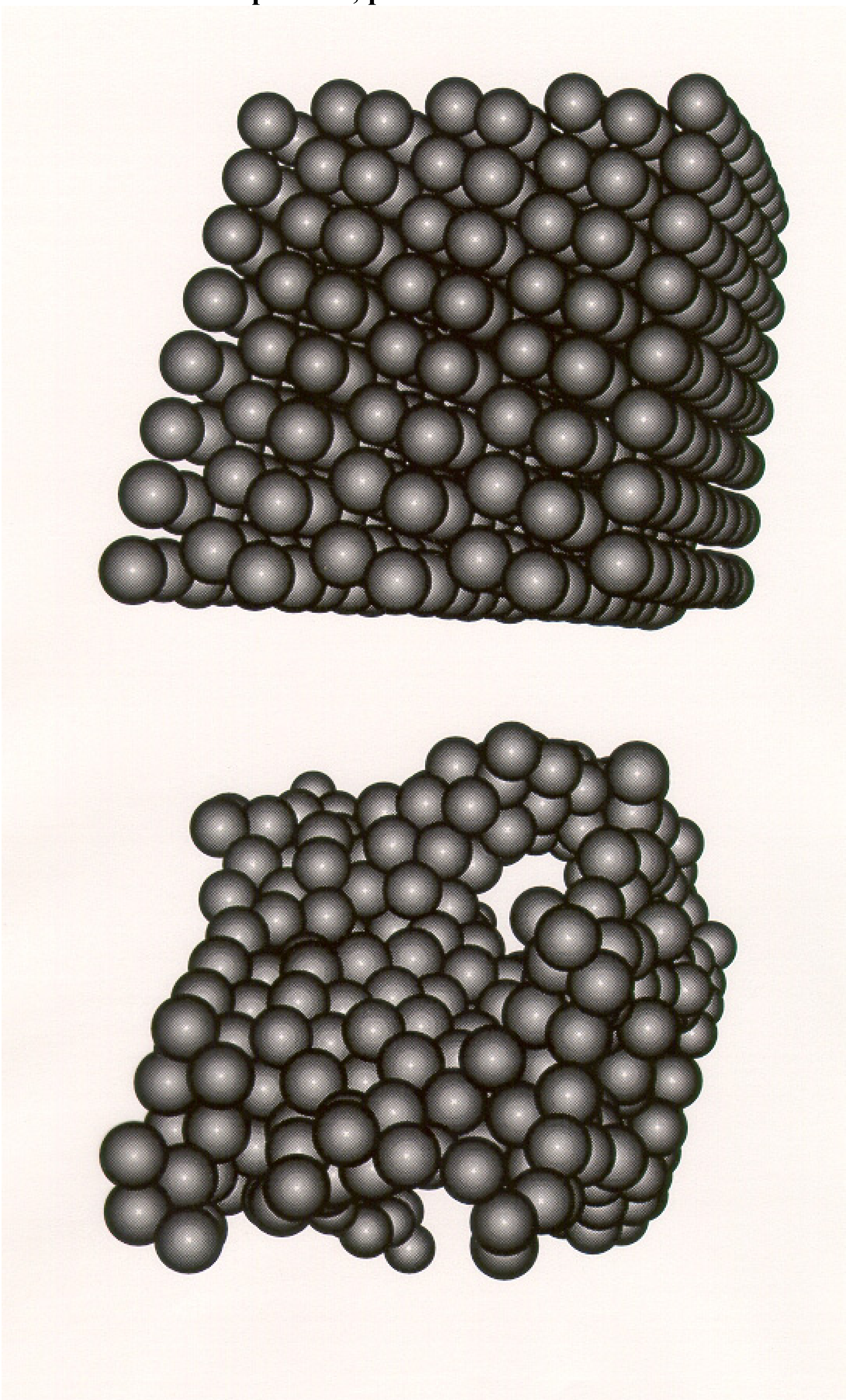
He^4 hcp lattice; porous inherent structure



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Crude estimate of p_s using liquid surface tension - water

Crude Estimate of p_S Using Liquid Surface Tension

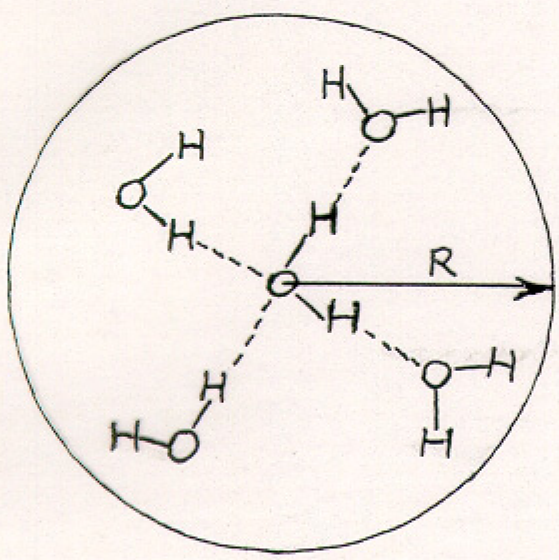
- Pressure difference between outside and inside of a bubble (Laplace formula):

$$\Delta p = p_{out} - p_{in} = -2\gamma / R \ ,$$

$$R = \text{radius}\ , \qquad \gamma = \text{surface tension}\ .$$

- "Bubble" approximation to mechanical weak spot in $T = 0$ amorphous medium at crucial density ρ_S:
  - (a) vacuum inside ($p_{in} = 0$), uniform density outside;
  - (b) R corresponds to a small number of molecules ($\approx 2 - 10$);
  - (c) requires $\gamma(T = 0)$ estimate for supercooled liquid.

- Numerical value choices for water:



$R \cong 4.0$ Angstroms,

$\gamma(T = 0) \cong 120$ dynes/cm.

$$\therefore\ p_S = -6.00 \text{ kbar}$$
$$= -27.5 p_c \ .$$

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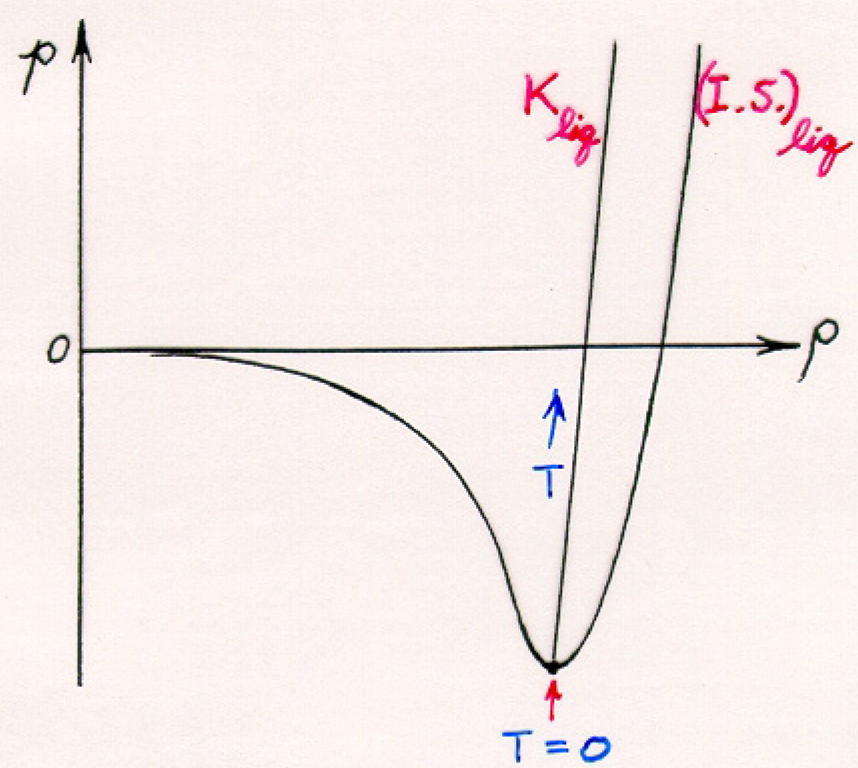
Kauzmann curves

KAUZMANN CURVES

- Defined to be the locus in the T,p plane on which the molar entropies of liquid and crystal phases (including metastable extensions) become equal: $\Delta S(T,p) = 0$.
- Established real examples: He^3, He^4, *poly(4-methylpentene-1)* .
- Likely candidates: "fragile" glass formers .
- Surprising results from theoretical models (repelling cores plus mean-field attractions): Low-T, low-p terminus of the Kauzmann curve is coincident with the liquid-phase inherent-structure pressure minimum.



Soft sphere model

SOFT SPHERE MODEL

- INVERSE-POWER PAIR POTENTIALS:

$$\Phi(\mathbf{r}_1 \ldots \mathbf{r}_N) = \varepsilon \sum_{i<j} (\sigma / r_{ij})^9 \quad .$$

- FCC CRYSTAL

- THERMODYNAMIC PRESSURE AND ENERGY DEPEND ON A FUNCTION OF A SINGLE DIMENSIONLESS VARIABLE

$$z = (\varepsilon / k_B T)^{1/3} \rho a^3 ,$$

$$\frac{p}{\rho k_B T} = 1 + u(z),$$

$$\frac{E}{N k_B T} = \frac{3}{2} + \frac{u(z)}{3} \quad .$$

- COEXISTENCE AT: $z_f = 1.334 \quad , \quad z_c = 1.373 \quad .$

- COMPUTER SIMULATION RESULTS:

$$u_f(z) \cong 7.13524 z^3 + \frac{1.72138 z}{3.37366 + z} + \frac{3.42602 z + 2.77862 z}{1.473 - 0.857 z + z^2}$$

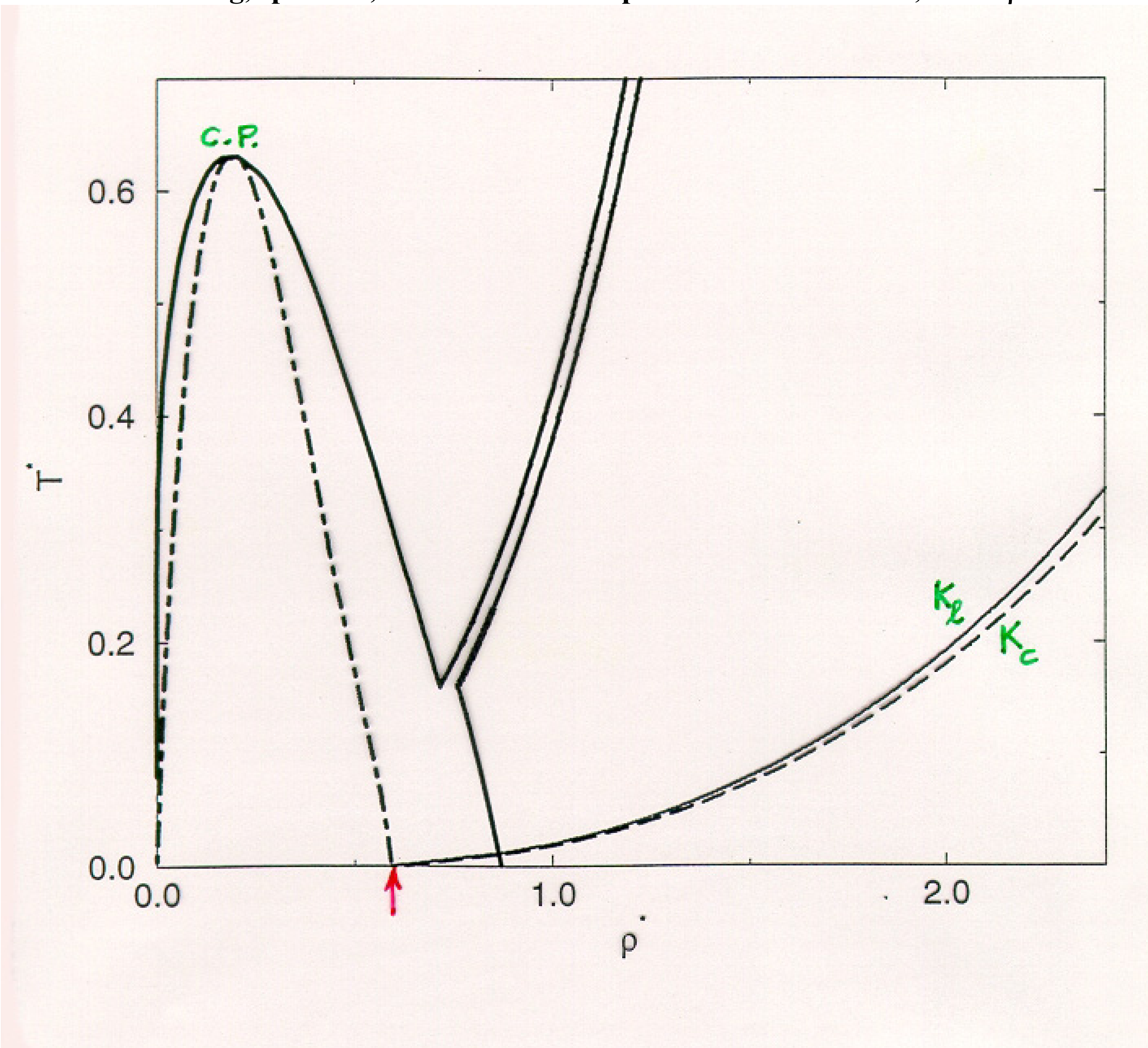
$$u_c(z) \cong 6.6252 z^3 + 4.5 \quad .$$

- INTEGRATE TO GET FLUID AND CRYSTAL ENTROPIES

- KAUZMANN CURVES IN ρ, T PLANE:

$$z_f^{(Kauz)} \cong 3.43 , \qquad z_c^{(Kauz)} \cong 3.50 \quad .$$

Coexisting, spinodal, K curves for soft sphere + m.f. attributes, T* vs ρ*



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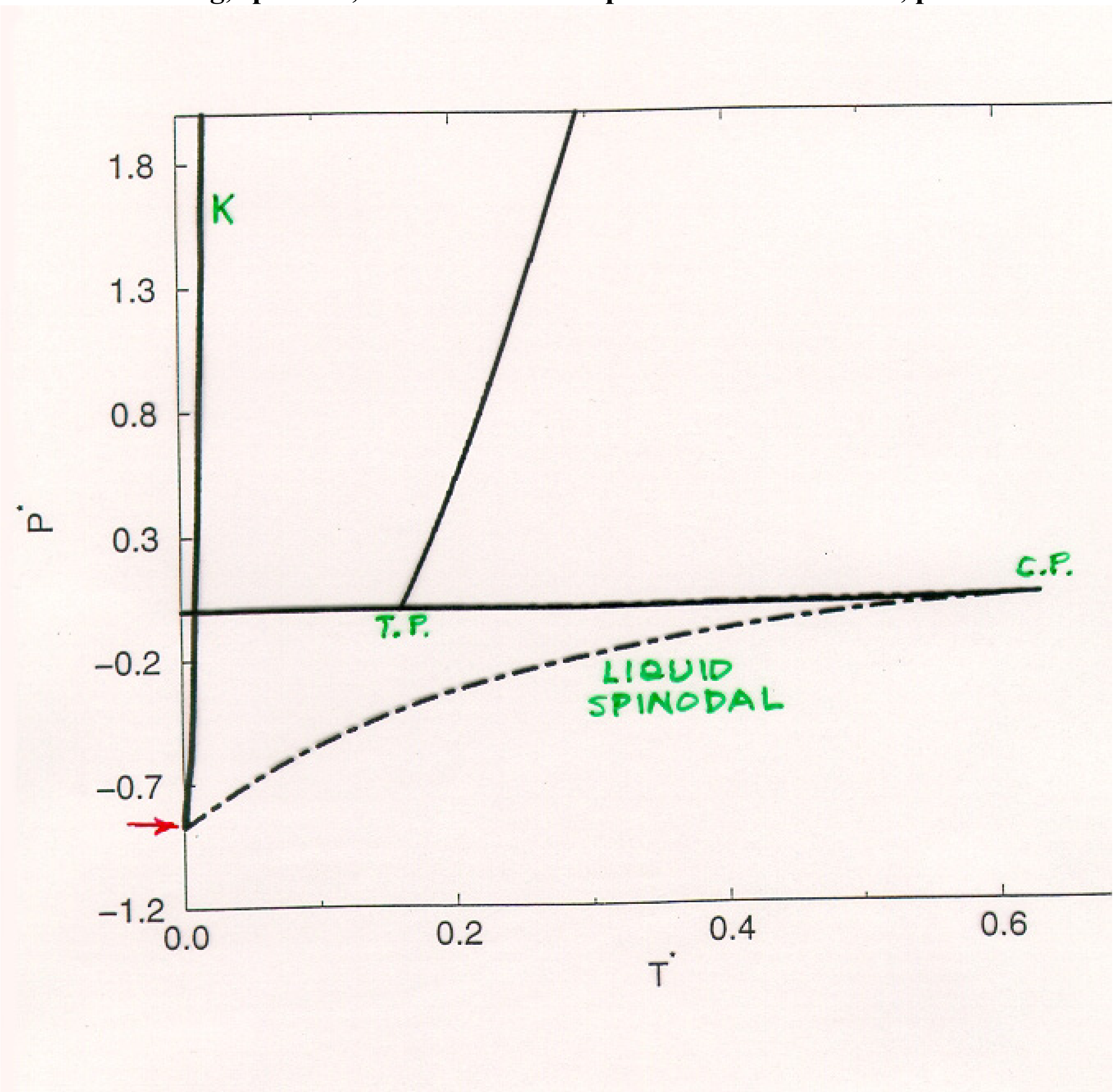
Coexisting, spinodal, K curves for soft sphere + m.f. attributes, p* vs T*



Tentative explanation

TENTATIVE EXPLANATION

- As $T \to 0$, the liquid spinodal loses significance as a locus of diverging density fluctuations.
- Maximally strong amorphous deposits must be devoid of weak spots (low-density, poorly-bonded regions).
- The constraints of local density and cohesive energy uniformity severely reduce the number of available IS's, and hence reduce both S_{str} and S_{vib} for the quenched liquid.
- The Kauzmann curve terminates at the lowest pressure that can be sustained by both crystal and amorphous phases. This is defined by the minimum of the amorphous-branch inherent structures (ρ_S, p_S).
- Consequently the spinodal and Kauzmann curves are able to approach a common point in the T, p plane as $T \to 0$.

Research topics

Research Topics

- Determine relation of isotropic-tension maximum strength parameters (ρ_S, p_S) to those describing strength limits for uniaxial stretch, shear.
- Find connection of ρ_S, p_S for binary mixtures (alloys) to those of the pure components.
- Formulate rules, if possible, for dependence of the dimensionless ratio p_S / p_c of substances on their chemical structures.
- Investigate "fractal" characteristics of aerogel-like inherent structures created from $\rho << \rho_S$ fluids. Is there a connection to DLA (diffusion-limited aggregation) processes?
- Revise, improve, and extend the crude surface tension estimate of p_S .
- Identify factors that quantitatively determine relative strengths of glass and crystal.
- Develop a more complete analysis of the $T \rightarrow 0$ connection between the liquid spinodal and the Kauzmann curve.