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

Frank H. Stillinger
Department of Chemistry, Princeton University, Princeton, NJ

1. Title and outline
2. Berthelot and Meyer experimental methods
3. Negative-pressure measurements for water
4. van der Waals equation of state
5. Mayer & Mayer reduced plot; $p_{\text{min}}(T=0) = -27p_c$
6. Virial equation of state
7. Virial equation of state - competing contributions
8. Effects (on $g^2(p)$) of mapping to inherent structures
9. Inherent structure "$T=0$ isotherms"
10. Illustrative model: 1D L-J system
11. Inherent structure energies vs. L/N, 1D L-J system
12. $p$(inh. str.) for 3D L-J system; $p_{\text{min}}/p_c = -30$
13. Fissured L-J configuration, N=1372
14. Two SPC/E water $p$(inh. str.) curves
15. Fissured SPC/E configuration
16. Vincent Shen's alkane results for $p$(inh. str.)
17. He$^4$ hcp lattice; porous inherent structure
18. Crude estimate of $p_s$ using liquid surface tension - water
19. Kauzmann curves
20. Soft sphere model
21. Coexisting, spinodal, K curves for soft sphere + m.f. attributes, $T^*$ vs $p^*$
22. Coexisting, spinodal, K curves for soft sphere + m.f. attributes, $p^*$ vs $T^*$
23. Tentative explanation
24. Research topics
Liquids and Glasses Under Tension

CHE 552 lecture, Tuesday, November 27, 2001 at Princeton University

Frank H. Stillinger
Department of Chemistry, Princeton University, Princeton, NJ

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.
Liquids and Glasses under Tension

Berthelot and Meyer experimental methods

LIQUIDS IN TENSION ($\sigma < 0$)

BERTHELOT METHOD:

Heat → COOL

$\sigma = \sigma_0 (T_0)$

$\sigma = \sigma_0 (T_1)$

$\sigma < 0$

MEYER'S PRESSURE MEASUREMENT:

MIRROR

HELICAL CAPILLARY
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:

\[ \rho \quad \frac{T \text{, } K}{0 \text{, } K} \]

Maximum tension observed: \( \approx -230 \text{ bar.} \)

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

References: L.J. Briggs, J. Appl. Phys. 21, 721 (1950);
Maximum tension observed: \(-277 \text{ bar.}\)

- Microscopic aqueous inclusions in quartz crystals imply maximum tension of \(-1400 \text{ bar at } 42^\circ \text{C. Reference: Q. Zheng, D.J. Durben, G.H. Wolf, and C.A. Angell, Science 254, 829 (1991).} \)
van der Waals Equation of State

- Conventional form:
  \[ p = \frac{Nk_BT}{V - Nb} \frac{N^2a}{V^2} \ . \]
  The “physical” region is \( V \geq Nb \) .

- Critical-point values:
  \[ p_c = \frac{a}{27b^2} \ , \quad k_BT_c = \frac{8a}{27b} \ , \quad v_c = \frac{V_c}{N} = 3b \ , \]
  \[ \frac{p_cv_c}{k_BT_c} = \frac{3}{8} \ . \]

- Reduced form ( \( p^* = p / p_c \), etc.):
  \[ p^* = \frac{8T^*}{3v^* - 1} - \frac{3}{v^{*2}} \ . \]

- Spinodal curves \( v^*_{sp}(T^*) \) determined by cubic polynomial:
  \[ v^* - (3v^* - 1)^2 / (4T^*) = 0 \ . \]

- Liquid spinodal becomes negative for \( T^* < \frac{27}{32} = 0.84375 \) .

F.H. Stillinger
Princeton University
11-27-01
Mayer & Mayer reduced plot; $p_{\text{min}}(T=0) = -27p_c$


Fig. 12.2. van der Waals equation. Plot of $P/P_c$ against $\nu/v_c$ for various values of $T/T_c$.

$$\frac{P}{P_c} = \frac{8(T/T_c)}{3(\nu/v_c) - 1} - \frac{3}{(\nu/v_c)^2}.$$ 

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

$$p_{\text{min}}(T = 0) = -27p_c$$
Virial Equation of State

- \( N \)-body system with pairwise-additive, spherically symmetric interactions:
  \[
  \Phi(r_1...r_N) = \sum_{i<j} \gamma(r_{ij})
  \]

- Virial equation for pressure in a thermal equilibrium state:
  \[
  p = \rho k_B T - \frac{2 \pi \rho^3}{3} \int_0^\infty r^3 v(r) g^{(2)}(r,\rho,T) dr
  \]
  \[
  p = N/V, \quad g^{(2)} = \text{pair correlation function}
  \]

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

- 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

- \[ p = \rho k_B T - \left(2\pi \rho^2 / 3\right) \int_0^\infty r^3 v(r) g^{(2)}(r, \rho, T) dr. \]

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

- 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.

- \( p_{\text{ideal}} \) 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:

\[ g^{(2)}_p \]

\[ f(r) \]

\[ g^{(2)}_{IS} \]

- Pre-mapping virial equation for pressure:

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

- Post-mapping version:

\[ p(\text{inh.str.}) = -(2\pi \rho^2 / 3) \int_0^\infty r^3 v'(r) g^{(2)}_{IS}(r, \rho) dr \]
Inherent Structure “T=0 Isotherms”

- Steepest-descent mapping on the $N$-body potential energy surface $\Phi$ relates any initial particle configuration to its parent inherent structure.
  
  $$\frac{d\mathbf{r}_j(s)}{ds} = -\nabla_{\mathbf{r}_j} \Phi(\mathbf{r}_1...\mathbf{r}_N) \quad (0 \leq s < \infty) .$$

- 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,
  
  $$p(\text{inh. strs.}) < p(\text{fluid}) .$$

- Graphical representation:

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

- $p(\text{inh. str.})$ 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, PERIODIC BOUNDARY CONDITIONS.

- POTENTIAL ENERGY FUNCTION:

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

\[ N(y) = 4(y^{-12} - y^{-6}). \]

- INHERENT STRUCTURES:

  A. \( 0 < L/N \leq \ell_0 \equiv 1.193 \Rightarrow \text{PERIODIC CHAIN}. \)

  B. \( \ell_0 < L/N \leq \ell_1 \equiv 1.2409 \Rightarrow \text{PERIODIC CHAIN, SINGLEY BROKEN}. \)

  C. \( \ell_1 < L/N \Rightarrow \text{SINGLY BROKEN CHAIN}. \)
Inherent structure energies vs. L/N, 1D L-J system
Liquids and Glasses under Tension

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

F.H. Stillinger
Princeton University
11-27-01

Inherent Structure Pressures

$\left( \text{L J} \right)$

Pressure (reduced units)

$\rho$

$P_{\text{min}}/p_c \approx -30$
Fissured L-J configuration, N=1372

\[ N = 1372 \]

\[ \rho^* = 0.725 , \quad T^*_{\text{initial}} = 0.9 \]
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 $p^{\text{IS}} (\rho)$ along isotherms of 260 K (circles) and 400 K (squares). The temperatures are those of the equilibrated liquid from which the inherent structures were obtained. A typical error bar is included in the upper left corner.
Fissured SPC/E configuration

SPC/E "WATER",

0.6 g/cm$^3$
Vincent Shen's alkane results for p(inh. str.)
He\textsuperscript{4} hcp lattice; porous inherent structure
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):
  $$\Delta p = p_{\text{out}} - p_{\text{in}} = -2\gamma / R,$$
  $$R = \text{radius}, \quad \gamma = \text{surface tension}.$$

- “Bubble” approximation to mechanical weak spot in $T = 0$ amorphous medium at crucial density $\rho_s$:
  (a) vacuum inside ($p_{\text{in}} = 0$), 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**:

  $$R \equiv 4.0 \text{ Angstroms},$$
  $$\gamma(T = 0) \approx 120 \text{ dynes/cm}.$$

  $$\therefore \quad p_s = -6.00 \text{ kbar} = -27.5p_s.$$
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: $\text{He}^3$, $\text{He}^4$, 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.

F.H. Stillinger
Princeton University
11-27-01
SOFT SPHERE MODEL

- INVERSE-POWER PAIR POTENTIALS:
  \[ \Phi(\mathbf{r}_1, ..., \mathbf{r}_N) = \varepsilon \sum_{i<j} (\sigma / r_{ij})^9 \]

- FCC CRYSTAL

- THERMODYNAMIC PRESSURE AND ENERGY DEPEND ON A FUNCTION OF A SINGLE DIMENSIONLESS VARIABLE
  \[ z = (\varepsilon / k_B T)^{1/3} \rho a^3, \]
  \[ p / \rho k_B T = 1 + u(z), \]
  \[ E / N k_B T = \frac{3}{2} + \frac{u(z)}{3} \]

- COEXISTENCE AT: \[ z_f = 1.334, \quad z_c = 1.373 \]

- COMPUTER SIMULATION RESULTS:
  \[ u_f(z) \approx 7.13524z^3 + \frac{1.72138z}{3.37366 + z} + \frac{3.42602z + 2.77862z}{1.473 - 0.857z + z^2} \]
  \[ u_c(z) \approx 6.6252z^3 + 4.5 \]

- INTEGRATE TO GET FLUID AND CRYSTAL ENTROPIES

- KAUFMANN CURVES IN \( \rho, T \) PLANE:
  \[ z_f^{(Kauf)} \approx 3.43, \quad z_c^{(Kauf)} \approx 3.50 \]
Coexisting, spinodal, K curves for soft sphere + m.f. attributes, $T^*$ vs $\rho^*$

F.H. Stillinger
Princeton University
11-27-01

Page 21
Coexisting, spinodal, K curves for soft sphere + m.f. attributes, p* vs T*
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 $(\rho_S, p_S)$.

- Consequently the spinodal and Kauzmann curves are able to approach a common point in the $T, p$ plane as $T \to 0$. 
Research Topics

- Determine relation of isotropic-tension maximum strength parameters \((\rho_S, p_S)\) to those describing strength limits for uniaxial stretch, shear.

- Find connection of \(\rho_S, p_S\) 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 \(\rho \ll \rho_S\) 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 \(T \to 0\) connection between the liquid spinodal and the Kauzmann curve.