A Toy Model
for
Viscosity

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Main References

C. A. Angell
*Formation of Glasses from Liquids and Biopolymers*,

T. Egami,
*Elementary Excitation and Energy Landscape in Simple Liquids*,

J. Bellissard
*Delone Sets and Material Science: a Program*,
Warning *This talk is reporting on a work in progress.*

1. Motivation
2. Anankeons and Phonons
3. Constructing the Model
4. Computing Maxwell’s Time
5. Conclusion
I - Motivation
Motivation

C. A. Angell,
“Formation of Glasses from Liquids and Biopolymers”,
Science, 267, No. 5206
Motivation

Motivation

Change of slope in Arrhenius behavior
Motivation

Comparison between the Maxwell relaxation time $\tau_M$ and the relaxation time $\tau_{LC}$ for local configurations.

Motivation

Specific Heat for Fragile Glasses


**Fig. 4.** Smoothed values of specific heats, $C_p$, of a $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$
Motivation

Specific Heat for Fragile Glasses:

contributions of phonons & anankeons
Motivation

- At temperature $T > T_{co}$ larger than the *crossover* temperature, only the *anankeons* contribute to the specific heat.

- If $T_{g} < T < T_{co}$ phonons and anankeon *interact*.

- **Question:** *How?*
Atomic Configurations

The set $\mathcal{L}$ of position of atomic nuclei is a Delone set, namely

- The *minimum distance* between atoms is $2r_0 > 0$.

- The *maximum diameter* of a *hole* without atoms is $2r_1 < \infty$. 
Atomic Configurations
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Atomic Configurations
Atomic Configurations
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Voronoï Cells

- Let $\mathcal{L}$ be Delone. If $x \in \mathcal{L}$ its Voronoi cell is defined by

$$V(x) = \{y \in \mathbb{R}^d ; |y - x| < |y - x'| \forall x' \in \mathcal{L}, x' \neq x\}$$

$V(x)$ is open. Its closure $T(x) = \overline{V(x)}$ is called the Voronoi tile of $x$
Voronoi Cells

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\( V(x) \) is open. Its closure \( T(x) = \overline{V(x)} \) is called the \textit{Voronoi tile} of \( x \)

**Proposition:** If \( \mathcal{L} \) is Delone, the Voronoi tile of any \( x \in \mathcal{L} \) is a convex polytope
Voronoï Cells

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$$V(x) = \{ y \in \mathbb{R}^d ; |y - x| < |y - x'| \forall x' \in \mathcal{L} , x' \neq x \}$$

$V(x)$ is open. Its closure $T(x) = \overline{V(x)}$ is called the Voronoi tile of $x$

**Proposition:** If $\mathcal{L}$ is Delone, the Voronoi tile of any $x \in \mathcal{L}$ is a convex polytope containing the closed ball $B(x; r_0)$ and contained in the ball $B(x; r_1)$
The Delone Graph

**Proposition:** the Voronoi tiles of a Delone set touch face-to-face
The Delone Graph

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Two atoms are *nearest neighbors* if their Voronoi tiles touch along a face of *maximal dimension*. 
The Delone Graph

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An *edge* is a pair of nearest neighbors. $\mathcal{E}$ denotes the set of edges.
The Delone Graph

**Proposition:** The Voronoi tiles of a Delone set touch face-to-face.

Two atoms are *nearest neighbors* if their Voronoi tiles touch along a face of *maximal dimension*.

An *edge* is a pair of nearest neighbors. $E$ denotes the set of edges.

The family $G = (L, E)$ is the Delone graph.
The Delone Graph

Fig. 1. Diagram of neighbourhood polyhedra, geometrical and physical, for two-dimensional arrays of points. (a) High co-ordinated; =, physical neighbours; (b) low co-ordinated; ...., geometrical neighbours

taken from J. D. Bernal, Nature, 183, 141-147, (1959)
The Delone Graph

Modulo graph isomorphism, the Delone graph encodes the local topology
Atomic Movements

**vibration**
*small, deterministic, conserves local topology*

**anankeon**
*large, unpredictable, quick jump, change the local topology*
III - Constructing the Model
Harmonic Motion

• The vibration of an atom around its equilibrium position is assumed to be harmonic.
• To simplify further, the oscillator will be supposed to be one-dimensional.
• The frequency \( \omega \) of the harmonic oscillator is defined by the curvature of the potential energy near the equilibrium position.
• Let \( q \) denotes the position of the harmonic particle relative to the equilibrium position. Then \( X \) will denote the phase space vector

\[
X = \begin{bmatrix} \omega q \\ q \end{bmatrix} = \begin{bmatrix} u \\ v \end{bmatrix}
\]
Harmonic Motion

- Equation of motion
  \[ m\frac{d^2q}{dt^2} + kq = 0, \quad \omega = \sqrt{\frac{k}{m}}. \]

- Equivalently
  \[ \frac{dX}{dt} = \omega JX, \quad \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \]

- Or else
  \[ X(t) = e^{\omega tJ}X(0) = \begin{bmatrix} \cos \omega t & \sin \omega t \\ -\sin \omega t & \cos \omega t \end{bmatrix} \begin{bmatrix} u(0) \\ v(0) \end{bmatrix} \]
Anankeon Interaction

- At *random times* \( \cdots < \tau_{n-1} < \tau_n < \tau_{n+1} < \cdots \), the atom *jumps quickly* from one potential well to another one.

- Each jump will be considered as *instantaneous*.

- In the new potential well, the *curvature is different*, hence, after the time \( \tau_n \), the new frequency is \( \omega_n \).

- After the jump, the new relative *phase space position is changed* by a vector \( \xi_n \), namely

\[
X(\tau_n + 0) = X(\tau_n - 0) + \xi_n
\]
Randomness: Assumptions

• The random times are *Poissonian*, namely the variables $\tau_{n+1} - \tau_n$ are *i.i.d*, with exponential distribution and average

$$\mathbb{E}\{\tau_{n+1} - \tau_n\} = \langle \tau_{n+1} - \tau_n \rangle = \tau_{LC}$$

• The frequencies $\omega_n$ are also *random* and *i.i.d*, such that

$$\mathbb{E}(\omega_n) = \omega, \quad \mathbb{E}\{(\omega_n - \omega)^2\} = \sigma^2$$

• The phase-space initial positions $\xi_n$ are also *random* and *i.i.d*, with *Gibbs distribution*

$$\text{Prob}\{\xi_n \in \Lambda\} = \int_{\Lambda} e^{-\beta m |\xi|^2 / 2} \frac{d^2 \xi}{2\pi k_B T/m'}, \quad \beta = \frac{1}{k_B T}$$
Correlation Function

• The goal is to compute the *stress-stress correlation function*. It is sufficient to compute

\[ C_f(t) = \mathbb{E}\{f(X(t))\overline{f(X(0))}\} \]

for any complex valued function \( f \) defined on the phase space and vanishing at infinity.

• The *viscosity* is given by the Green-Kubo formula

\[ \eta = \frac{V}{k_B T} \int_0^\infty C_f(t) \, dt \]

for a suitable \( f \).
Correlation Function

• Then, the goal is to show that

\[ C_f(t) \xrightarrow{t \to \infty} e^{-t/\tau_M} \]

• Hence \( \eta \sim \tau_M \), which allows to interpret \( \tau_M \) as the Maxwell relaxation time.
Correlation Function

• The *dissipative evolution* operator $P_t$ acting on the set of functions $f$ is defined by

$$P_t f(x) = \mathbb{E}\{f(X(t)) | X(0) = x\}$$

• Then

$$C_f(t) = \int_{\mathbb{R}^2} f(x) P_t f(x) \, d^2x$$
IV - Computing Maxwell’s Time
Laplace Transform

- The Laplace transform of \( C(t) \) is defined by

\[
\mathcal{L}C(\zeta) = \int_{0}^{\infty} e^{-t\zeta} C(t) \, dt
\]

- The function \( C \) admits the asymptotic \( C(t) \uparrow_{\infty} e^{-t/\tau_M} \) if and only if

\( \mathcal{L}C(\zeta) \) is holomorphic w.r.t. \( \zeta \) in the domain \( \Re \zeta > -1/\tau_M \)

- In practice, \(-1/\tau_M\) is the singularity nearest to the origin in the complex plane.
Dual Actions

• **Phase Space Rotation:** If \( f \) is a function, and \( x = (u, v) \) a point in the phase space, then

\[
f \left( e^{\omega t} J x \right) = \left( e^{-\omega t} J f \right)(x), \quad -J = v \partial_u - u \partial_v
\]

Hence \( J \) is the *phase-space angular momentum*.

• **Phase Space Translation:** Similarly, if \( \xi = (\xi^1, \xi^2) \) is a phase-space vector,

\[
f(x + \xi) = \left( e^{\xi \cdot \nabla} f \right)(x), \quad \xi \cdot \nabla = \xi^1 \partial_u + \xi^2 \partial_v
\]

Hence \( \xi \cdot \nabla \) is the *phase-space momentum* along the vector \( \xi \).
Stochastic Evolution

• Let $X(t)$ the stochastic value of the *phase-space position* at time $t$, with initial condition $X(0) = x$.

• If $n$ anankeons occurred during this time then $\tau_n \leq t < \tau_{n+1}$, with $\tau_0 = 0$, so that

$$f(X(t)) = \left\{ \prod_{j=1}^{n} \left( e^{-\left(\tau_j - \tau_{j-1}\right)\omega_{j-1}} e^{\xi_j \cdot \nabla} \right) e^{-(t-\tau_n)\omega_n} f \right\}(x)$$

• In this expression the the $\tau_j - \tau_{j-1}$'s, the $\omega_j$'s and the $\xi_j$'s are *random, independent and identically distributed*. 
**Stochastic Evolution**

- **Averaging** and taking the Laplace transform leads to

\[ \mathcal{L}P_\zeta f(x) = \int_0^\infty e^{-t\zeta} P_t f(x) \, dt, \quad \zeta \in \mathbb{C} \]

- Equivalently

\[ \mathcal{L}P_\zeta f(x) = \mathbb{E}\left\{ \sum_{n=0}^{\infty} \int_{\tau_n}^{\tau_{n+1}} e^{-t\zeta} \prod_{j=1}^{n} \left( e^{-(\tau_j - \tau_{j-1})\omega_{j-1}\mathbb{J}} \, e^{\xi_j \cdot \nabla} \right) e^{-(t - \tau_n)\omega_n\mathbb{J}} f(x) \, dt \right\} \]

- **Remark:** \( \tau_0 = 0 \), thus \( t = t - \tau_n + (\tau_n - \tau_{n-1}) + \cdots + (\tau_1 - \tau_0) \). Hence \( \omega_{j-1}\mathbb{J} \) can be replaced by \( \omega_{j-1}\mathbb{J} + \zeta \) and the exponential pre-factor \( e^{-t\zeta} \) disappears.
Stochastic Evolution

- First evaluate the integral over time between $\tau_n$ and $\tau_{n+1}$, by setting $s = t - \tau_n$

$$\int_0^{\tau_{n+1} - \tau_n} e^{-s\zeta} e^{-s\omega_n} ds = \frac{1 - e^{(\tau_{n+1} - \tau_n)(\zeta + \omega_n)}}{\zeta + \omega_n}$$

- Second, average over the $\tau_j - \tau_{j-1}$'s, using the formula (here $A$ is an operator)

$$\mathbb{E}_\tau \{ e^{-(\tau_j - \tau_{j-1})A} \} = \int_0^\infty e^{-s/\tau_{LC} - sA} \frac{ds}{\tau_{LC}} = \frac{1}{1 + \tau_{LC}A}$$
Stochastic Evolution

• **Reminder:** if two random variables $X, Y$ are *stochastically independent* then $\mathbb{E}\{XY\} = \mathbb{E}\{X\} \mathbb{E}\{Y\}$.

• The average over the $\tau_j - \tau_{j-1}$’s gives

\[
\mathcal{L}P_{\xi}f(x) = \tau_{LC} \sum_{n=0}^{\infty} \mathbb{E}\left\{ \prod_{j=1}^{n} \left( \frac{1}{1 + \tau_{LC}(\zeta + \omega_{j-1})} e^{\xi_j V} \right) \frac{1}{1 + \tau_{LC}(\zeta + \omega_n)} f(x) \right\}
\]

• This gives a new averaging over a product of *independent* variables.
Stochastic Evolution

- **Averaging** over the $\xi_j$’s can be done using (Gibbs average is a Gaussian integral)

$$\mathbb{E}_\xi \left\{ e^{\xi_j \cdot \nabla} \right\} = e^{k_B T \Delta / 2m}, \quad \Delta = \nabla \cdot \nabla = \partial_u^2 + \partial_v^2$$

- **Averaging** over the $\omega_j$’s leads to defining the following operator

$$A(\zeta) = \mathbb{E} \left\{ \frac{1}{1 + \tau_{LC}(\zeta + \omega_{j-1}|J)} \right\}$$

- **Remark:** $A(\zeta)$ does not depend on $j$ since all the $\omega_j$’s have same distribution.
• **Inserting** into the expression of the Laplace transform leads to

\[
\Omega P_\zeta f(x) = \tau_{LC} \sum_{n=0}^{\infty} \left\{ A(\zeta) e^{k_B T \Delta/2m} \right\}^n A(\zeta) f(x)
\]

\[
= \tau_{LC} \frac{1}{1 - A(\zeta) e^{k_B T \Delta/2m}} A(\zeta) f(x)
\]

• **Questions:**
  
  – How do we evaluate this function?
  – How can we compute the *domain of analyticity* in $\zeta$?
Angular Momentum

• **Trick:** the operator $A(\zeta)$ is a function of the phase-space angular momentum $J$.

• The *polar coordinates* in the 2D-phase space are given by

\[
\begin{align*}
    u &= r \cos \theta \\
    v &= r \sin \theta
\end{align*}
\]

\[\Leftrightarrow\]

\[
\begin{align*}
    r^2 &= u^2 + v^2 \\
    \tan \theta &= v/u
\end{align*}
\]

• It follows that

\[
J = \frac{\partial}{\partial \theta}
\]
Angular Momentum

• Consequently the eigenvalues of $J$ are given by $\imath \ell$ with $\ell = 0, \pm 1, \pm 2, \cdots$, namely $\ell \in \mathbb{Z}$.

• The eigenfunctions have the form

$$g_\ell(r, \theta) = \hat{g}_\ell(r) e^{\imath \ell \theta}$$

• Projecting a function $f$ onto the eigenspace of eigenvalue $\imath \ell$ is given by

$$\Pi_\ell f(r, \theta) = e^{\imath \ell \theta} \int_{0}^{2\pi} f(r, \theta) e^{-\imath \ell \theta} \frac{d\theta}{2\pi}$$

• Hence the spectral decomposition gives

$$J = \sum_{\ell \in \mathbb{Z}} \imath \ell \Pi_\ell$$
Angular Momentum

• Any function of $\mathbf{J}$ can be written as

$$F(\mathbf{J}) = \sum_{\ell \in \mathbb{Z}} F(\imath \ell) \, \Pi_{\ell}$$

• It leads to

$$A(\zeta) = \sum_{\ell \in \mathbb{Z}} a_{\ell}(\zeta) \, \Pi_{\ell}$$

with $a_{\ell}(\zeta)$ a complex number given by

$$a_{\ell}(\zeta) = \mathbb{E}_\omega \left\{ \frac{1}{1 + \tau_{lc}(\zeta + \imath \ell \omega_j)} \right\}$$
Angular Momentum

• **New Trick:** the operator $\Delta$ commutes with $J$, more precisely, the polar decomposition gives

$$\Delta = -p_r^2 + \frac{J^2}{r^2} - p_r^2 = \partial_r^2 + \frac{1}{r} \partial_r$$

• This gives

$$\mathcal{L} P_{\zeta} = \tau_{lc} \sum_{\ell \in \mathbb{Z}} \frac{1}{1 - a_{\ell}(\zeta)e^{-k_B T (p_r^2 + \ell^2/r^2)}} a_{\ell}(\zeta) \Pi_{\ell}$$
Analyticity

• Remark that if $\omega > 0$ the function $(1 + \tau_{LC}(\zeta + i\ell\omega))^{-1}$ admits a pole at

$$\zeta = -\frac{1}{\tau_{LC}} - i\ell\omega$$

• It follows that $a_\ell(\zeta)$ is analytic in $\Re(\zeta) > -1/\tau_{LC}$

• The operator $p_r^2 + \ell^2/r^2$ is positive, and its spectrum is the entire positive real line. Hence, $\mathcal{P}_\zeta$ is analytic in the domain for which there is no $\ell \in \mathbb{Z}$ nor any $p \geq 0$ such that $a_\ell(\zeta) = e^{p^2} \geq 1$.

It means the set of $\zeta$ must satisfy $a_\ell(\zeta) \notin [1, \infty)$.
The domain of analyticity of $a_l(\zeta)$ is given by $\Re \zeta > -1/\tau_{LC}$. 
Analyticity

• The *correlation function* for $X(t)$ involves only the angular momentum $\ell = \pm 1$.

• Assume that the distribution of $\omega_j$ is *uniform* with average $\omega$ and variance $\sigma$. Then the $\omega_j$'s are uniformly distributed in the interval $[\omega - \sqrt{3} \sigma, \omega + \sqrt{3} \sigma]$ and

$$a_{\pm 1} = \frac{1}{2i \sqrt{3} \tau_{LC} \sigma} \ln \left( \frac{1 + \tau_{LC}(\zeta + i\omega + i\sqrt{3}\sigma)}{1 + \tau_{LC}(\zeta + i\omega - i\sqrt{3}\sigma)} \right)$$

• If $\zeta + i\omega$ is *not real*, then the imaginary part of the r.h.s. is non zero, so that $a_{\pm 1} \notin [1, \infty)$. 
Analyticity

• If $\xi = \zeta + i\omega$ is real then

$$a_{\pm 1} = \frac{1}{2i \sqrt{3}\tau_{LC}\sigma} \ln \left( \frac{1 + \tau_{LC}(\zeta + i\omega + i\sqrt{3}\sigma)}{1 + \tau_{LC}(\zeta + i\omega - i\sqrt{3}\sigma)} \right) = \frac{\theta}{\sqrt{3}\tau_{LC}\sigma}$$

where

$$\tan \theta = \frac{\sqrt{3}\tau_{LC}\sigma}{1 + \tau_{LC}\xi} \quad |\theta| < \frac{\pi}{2}$$
Maxwell Relaxation Time

- After some algebra, this gives

\[ \tau_M = \begin{cases} 
\tau_{LC} & \text{if } \sqrt{3}\tau_{LC}\sigma \geq \pi/2 \\
\tau_{LC}\left(1 - \frac{\sqrt{3}\tau_{LC}\sigma}{\tan \sqrt{3}\tau_{LC}\sigma}\right)^{-1} & > \tau_{LC} \text{ otherwise}
\end{cases} \]

- Using a uniform distribution of oscillator frequencies is a reasonable approximation. If \( \tau_{LC}\sigma \) decreases to zero as \( T \downarrow 0 \), then
  - This gives a crossover temperature \( T_{co} \) above which the anankeon dominates and \( \tau_{LC} = \tau_M \) for \( T \geq T_{co} \)
  - If \( T < T_{co} \), the phonons resist and \( \tau_M/\tau_{LC} > 1 \).
The variance $\sigma$ of the random frequencies depend upon the modification of the local landscape by anankeons. However, each anankeon involves several atoms, at least $d + 2$ atoms in dimension $d$. So the landscape is modified in a region that might be large compared with the mean atomic distance.

For this reason, $\sigma$ is expected to be proportional to a Gibbs factor, namely to follow also an Arrhenius law

$$\sigma = \sigma_\infty e^{-W_v/k_B T} \quad \sigma_\infty = \lim_{T \to \infty} \sigma(T)$$

**Question:** What is the meaning of $W_v$?
Maxwell Relaxation Time

• Similarly the local configuration time $\tau_{LC}$ is also given by a similar expression, thanks to Kramers formula, where now $W$ is the potential energy barrier to be crossed when an anankeon occurs

$$\tau_{LC} = \tau_\infty \ e^{W/k_BT} \quad \tau_\infty = \lim_{T \to \infty} \tau(T)$$

• If the hypothesis made on $\sigma$ is correct, then

$$K(T) = \tau_{LC}(T)\sigma(T) = K_\infty \ e^{-(W_v-W)/k_BT} \quad K_\infty = \sigma_\infty \ \tau_\infty$$

The condition $K(T) \xrightarrow{T \downarrow 0} 0$ requires $W_v > W$
Maxwell Relaxation Time

- Hence, if $T_g < T < T_{co}$

\[
\frac{\tau_M}{\tau_{LC}} = \frac{1}{1 - \frac{\sqrt{3}K(T)}{\tan(\sqrt{3}K(T))}} \quad T \downarrow 0 \quad e^{2(W_v - W)/k_BT} \sim \frac{e^{2(W_v - W)/k_BT}}{K_\infty^2}
\]

- Similarly the crossover temperature is reached whenever $\sqrt{3}\tau_{LC}\sigma = \pi/2$, which gives

\[
(W_v - W) = \frac{k_BT_{co}}{10.2}
\]
V - Conclusion
To Summarize

- The liquid phase of *fragile glasses* is dominated by *anankeons* at least above the crossover temperature $T > T_{co}$.
- If $T_g < T < T_{co}$, the *phonon-anankeon interaction* becomes essential to explain the difference between the Maxwell and the local configuration times. Hence the change of the Arrhenius behavior of the viscosity is explained through a *dynamical effect*. As the temperature decreases, phonons become more coherent and *limit the dissipative* effect of the anankeons.
- The crossover temperature is related to the difference $W_s - W$ between the activation energies associated with the *phonon frequency fluctuation* and the *anankeon potential barrier*. 