Day Three

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Density functional theory $\leftrightarrow$ Random First Order

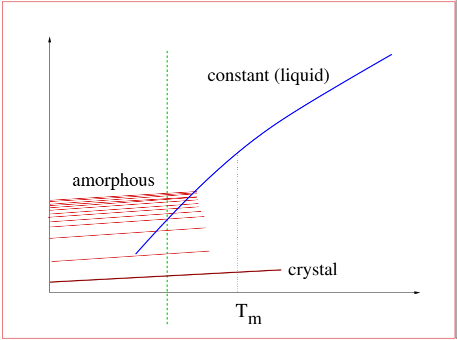
a mean-field free energy

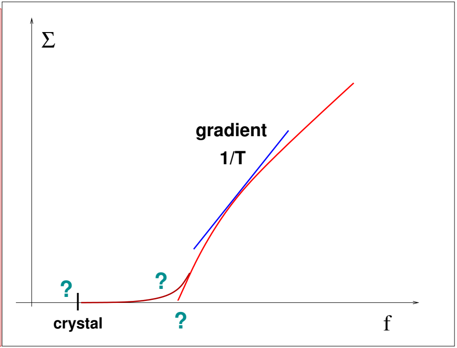
$$F[\rho(\mathbf{x})] = \int d^3\mathbf{x}\ \rho[\ln\rho(\mathbf{x}) - 1] - \frac{1}{2}\int d^3\mathbf{x}\ d^3\mathbf{x}'\ [\rho(\mathbf{x}) - \rho_o] C(\mathbf{x}-\mathbf{x}') [\rho(\mathbf{x}') - \rho_o]$$

has many local minima, solutions of

$$\frac{\delta F[\rho(\mathbf{x})]}{\delta \mathbf{x}} = \ln\rho(\mathbf{x}) - 1 - \int d^d\mathbf{x}'\ C(\mathbf{x}-\mathbf{x}', \rho_o)[\rho(\mathbf{x}') - \rho_o] = 0$$

liquid – crystal + many amorphous





The freezing at the Kauzmann temperature

$$\mathbf{Z} = \mathbf{\Sigma}_{\mathbf{solutions}} \quad \mathbf{e}^{\mathbf{V}[\mathbf{\Sigma}(\mathbf{f}) - \beta \mathbf{f}]}$$

$$\frac{\mathbf{d\Sigma}}{\mathbf{df}} = \frac{\mathbf{1}}{\mathbf{T}}$$

Density functional theory $\leftrightarrow$ Random First Order

we may simplify even further, just as going from Landau theory to Curie-Weiss:

$$F[\rho(\mathbf{x})] = \int d^3\mathbf{x}\ \rho[\ln \rho(\mathbf{x}) - 1] - \frac{1}{2} \int d^3\mathbf{x}\ d^3\mathbf{x}'\ [\rho(\mathbf{x}) - \rho_o] C(\mathbf{x} - \mathbf{x}') [\rho(\mathbf{x}') - \rho_o]$$

$$\downarrow$$

$$E[\rho_1, ..., \rho_N] = \sum_{ijk} J_{ijk} \rho_i \rho_j \rho_k$$

has similar phenomenology

Here, I am cutting a long story short.

- This form of density functional theory was introduced long ago (70's), and used to study crystallisation

- Later the existence of amorphous solutions, and hence the relevance for glasses, was remarked (1984).

- Random First Order theory started from the observation that spin glass-like models with quenched disorder $E = \sum_{ijk} J_{ijk} s_i s_j s_k$ where mean-field models of glasses (late 80's)

- This led to an explosion of results (mainly in the 90's), because well established techniques *(and technicians)* where now available.

- Finally, one may come back to a local mean-field (Landau) theory for $\rho(x)$, which will be a better-understood and consistent form of density functional theory. The phenomenological (for the moment) extension beyond mean-field is the subject of the mosaic theory.

The thermodynamics, and indeed all landscape features may be obtained from Parisi (replica) theory

the Kauzmann temperature appears as a Replica Symmetry Breaking (freezing) transition

The dynamics associated with these models

$$\ddot{\rho}_i = -\frac{\partial E}{\partial \rho_i} \; + \; thermal \; bath$$

is also exactly solvable

- Above T_c the system equilibrates in finite time - Mode Coupling Equations
- Below T_c the system never equilibrates. It ages.

- **The appearance of effective temperatures:**

Correlation and response functions obey the exact equation

$$R(t,t_w) \equiv \left.\frac{\delta s(t)}{\delta h(t_w)}\right|_{h=0} , \qquad \chi(t,t_w) \equiv \int_{t_w}^{t} dt'\, R(t,t') \,.$$

$$\begin{aligned}
\frac{\partial C(t,t_w)}{\partial t} &= \left(-\mu(t) C(t,t_w) + \int_0^{t_w} dt'' C^p(t,t'') R(t_w,t'')\right) \\
&\quad + \int_0^t dt'' C^{p-1}(t,t'') R(t,t'') C(t'',t_w) \,, \\
\frac{\partial R(t,t_w)}{\partial t} &= \left(-\mu(t) R(t,t_w) + \int_{t_w}^{t} dt'' C^{p-1}(t,t'') R(t,t'') R(t'',t_w)\right) \,.
\end{aligned}$$

In equilibrium, they reduce to the Mode Coupling Equations

$$\frac{\partial C(t-t_w)}{\partial t} = -\mu\, C(t-t_w) + \frac{1}{T}\int_{t_w}^{t} dt''\; C^p(t-t'')\; \frac{\partial C(t''-t_w)}{\partial t''} + c$$

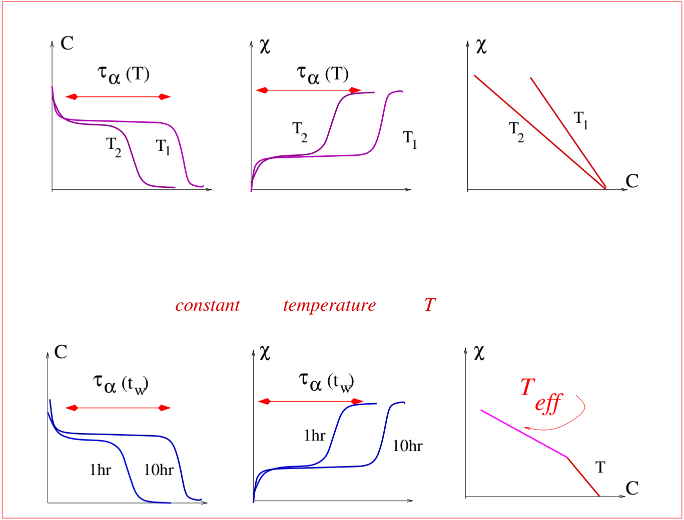
The Mode Coupling equations have a transition temperature where the timescale diverges as a power law

this Mode-Coupling transition is an artifact, destroyed by fluctuations

Below the transition temperature

the system ages **forever**

Above and below the transition



Random First Order theory is at present the best bet

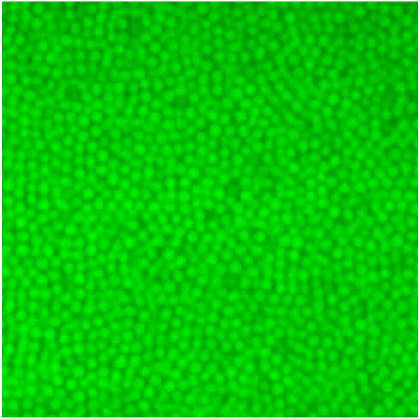
but going beyond mean-field is at the same time necessary and daunting

Is there ***purely geometric*** order in a ***solid***?

i.e. an order that can be read from a configuration, without knowing the interactions or dynamics

just as in crystals or quasicrystals

Remember: solid = spatial density modulations not erased by thermal fluctuations

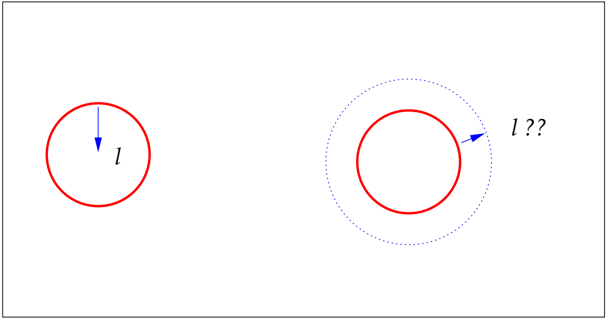


Liquid or Glass ?

A Theorem for point-to-set correlations **Montanari-Semerjian**

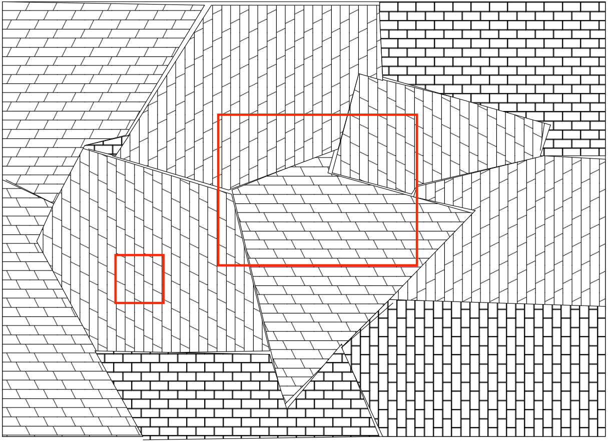
boundary determines interior for $\ell < \ell(T)$

$\ell \to \infty$ **if (**$timescale \quad \to \infty$**)**

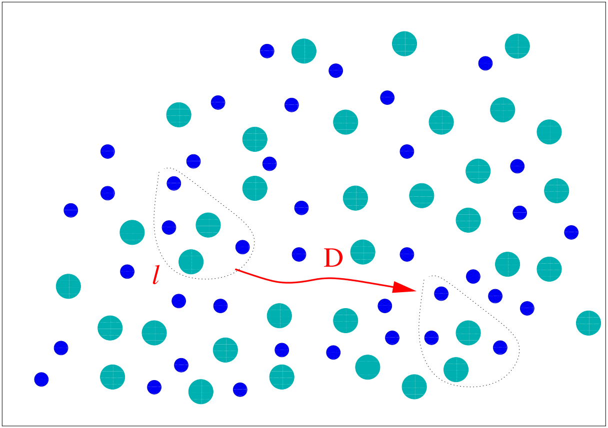


Patch - recurrence length $D(l)$ crossover l_o

detects crystallite length.



Generalize this to general systems



Perfect order (three kinds)

Three levels of order

0101010101010101010101010101

Periodic, *Fourier transform gives deltas.*

1011010110110101101011011010110110

Fibonacci sequence *Quasiperiodic, Fourier transfom → dense set of δ-functions*

01101001100101101001011001101001

Thue-Morse sequence *'Non-Pisot" Fourier transform has no δ functions.*

Patch repetition is a matter of entropy

subextensive entropy $\rightarrow$ infinite length

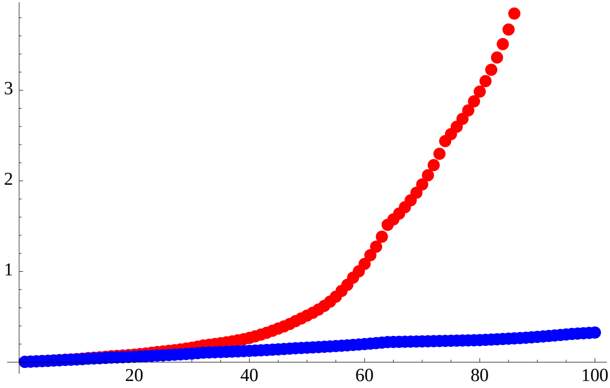
independent pieces will always yield extensive entropy

Finite correlation lengths in imperfect sequences

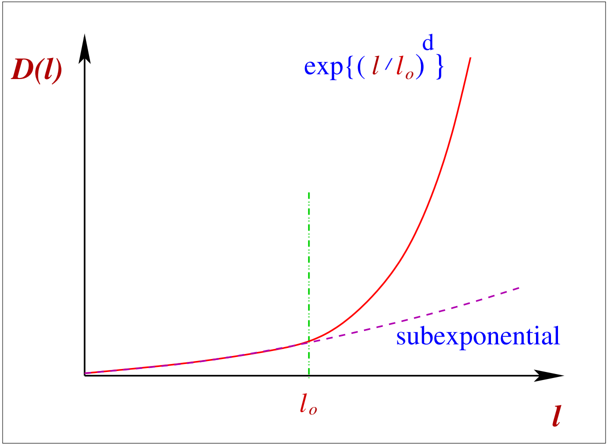
$D(l)$ vs. l

11001011010010110010110011010000101101001011101101001100

11001011010010110010110011010000101101001011101101001100

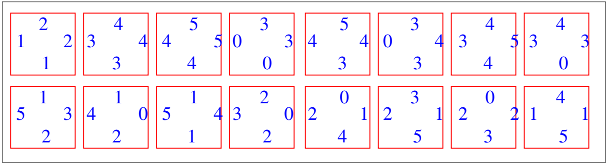


Patch - recurrence length $D(l)$ crossover l_o



More examples: higher dimensionalities

Wang Tiles

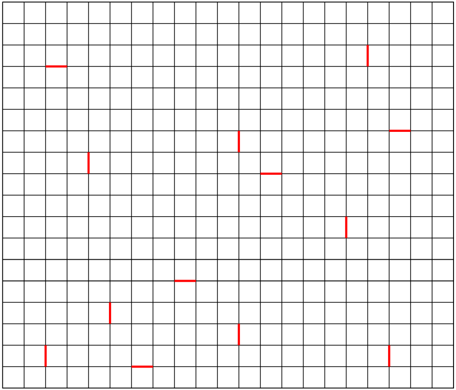


Quasiperiodic ground states

can be seen as a 12-state spin model (Leuzzi and Parisi)

Monte Carlo dynamics is slow

annealing to zero temperature leads to a system with point defects

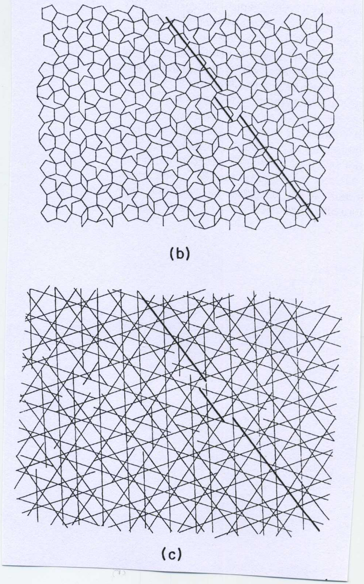


coherence length = inter-defect lenght!!!

Note that coherence is lost through energetically pointlike defects

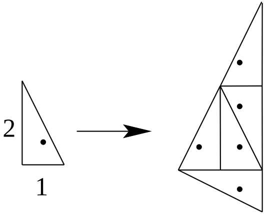
There is a way to see this, through the Ammann lines.

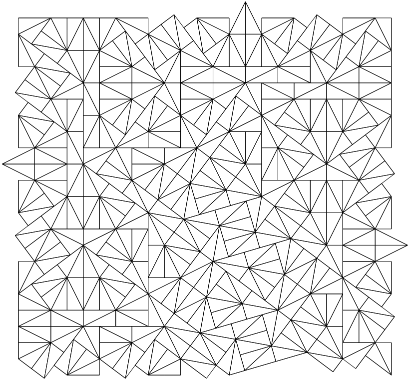
For example, in a true quasicrystal, one can see this: (Li, Zhang and Kuo):



An amorphous Pinwheel tiling

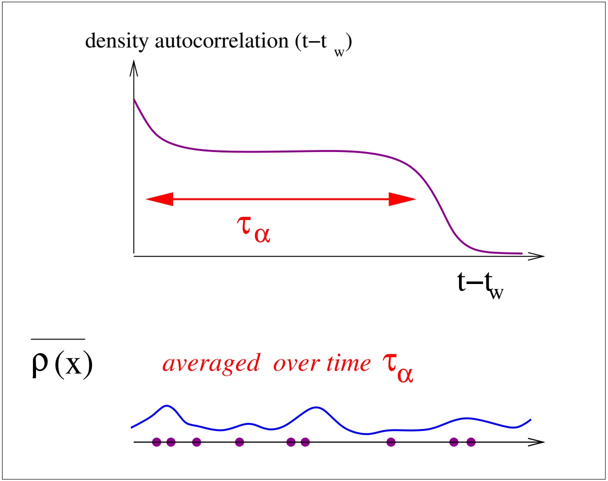
of Radin and Conway (fig: Baake, Frettlöh and Grimm)



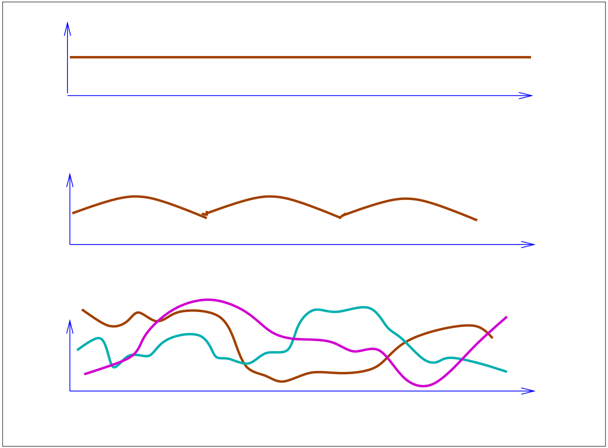


again, infinite coherence length

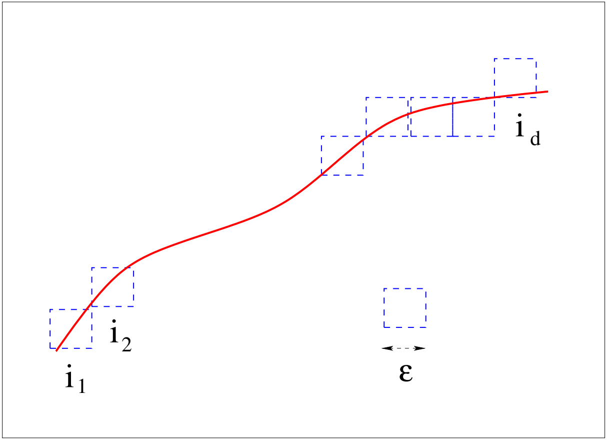
Particle systems: supercooled liquid



Average density profiles: constant, periodic, 'chaotic'



We need to count profiles $\leftrightarrow$ identify patches



inspiration from dynamic systems

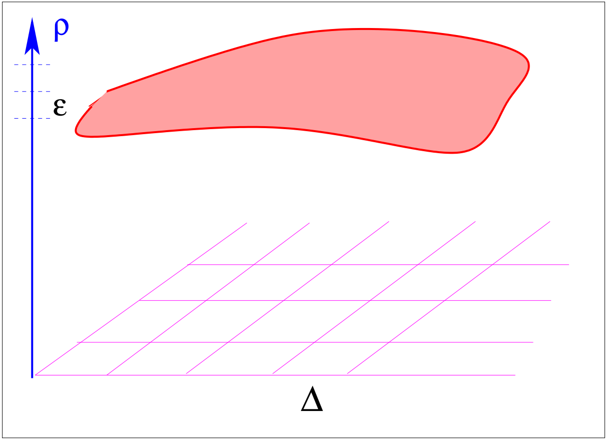
The limit is well-defined:

$$K_1 \sim - \lim_{\tau \to 0} \lim_{\epsilon \to \infty} \lim_{d \to \infty} \frac{1}{\tau d} \sum_{i_1,\ldots,i_d} P_\epsilon(i_1, \ldots, i_d) \ln P_\epsilon(i_1, \ldots, i_d)$$

Renyi: a measure of 'rare' patches (very frequent or very unfrequent):

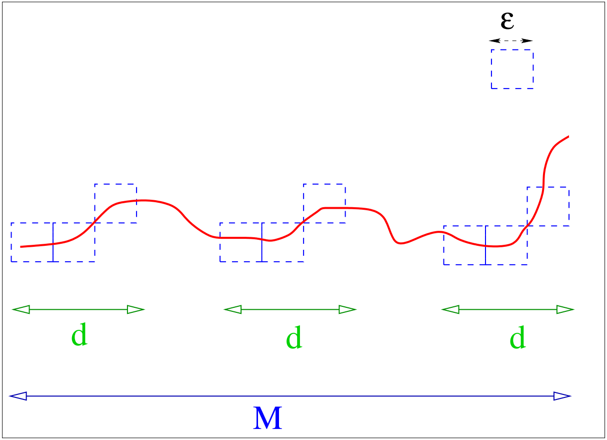
$$K_q \sim - \lim_{\tau \to 0} \lim_{\epsilon \to \infty} \lim_{d \to \infty} \frac{1}{\tau d(q-1)} \ln \left(\sum_{i_1,\ldots,i_d} P_\epsilon(i_1, \ldots, i_d)^q \right)$$

$\ldots \to \mathcal{P}[P_\epsilon]$ **by Legendre transform.**



$$t \to \vec{r} \qquad x \to \rho$$

Grassberger-Procaccia:



count the number of repetitions n_i of a patch of size d within a large box M and average over patches

$$P_\epsilon(i_1, ..., i_d)^q \sim \frac{1}{M} \sum_i [n_i^d(\epsilon)]^{q-1} \sim \epsilon^\phi \; e^{\tau(q-1)d \, K_q}$$

So that:

$$K_d \sim \lim_{\tau \to 0} \lim_{\epsilon \to \infty} \lim_{d \to \infty} \frac{1}{\tau(q-1)} \frac{\delta}{\delta d} \ln \left[\sum_i [n_i^d(\epsilon)]^{q-1} \right]$$

for K_1 we use $[\sum_i \ln[n_i^d(\epsilon)]]$

practical because we work at finite precision

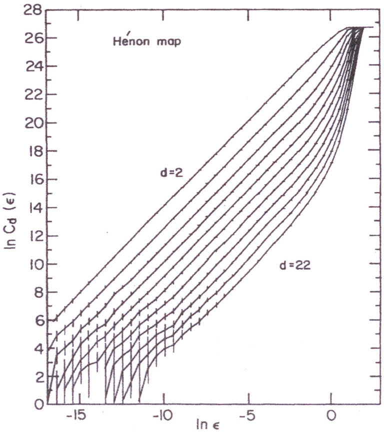


FIG. 3. Same as Fig. 1, but for the Hénon map. The values of d are $d=2$ (top curve), 4,6,8, . . . ,22 (bottom curve).

Now, let us argue that if the timescale goes to infinity

in any super-Arrhenius manner

complexity is necessarily subextensive

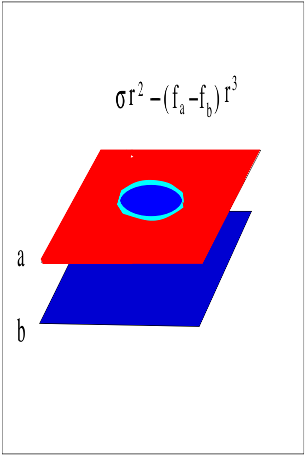
- **and lengthscale goes to infinity**

Two nucleation arguments show that it is impossible to have stable states

- **with free energy density higher than equilibrium**

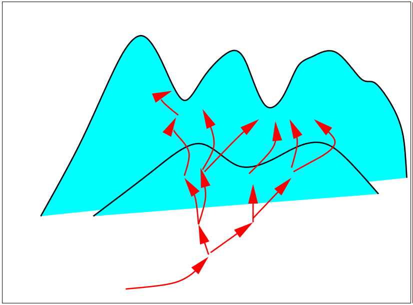
or

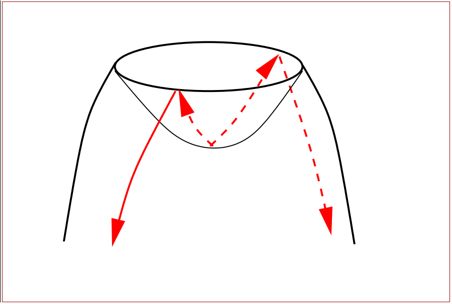
- **exponential in number**



$$r^* = \frac{(2)\sigma}{3(f_a - f_b)} \quad \rightarrow \quad f(r^*) \propto \frac{\sigma^3}{(f_a - f_b)^2}$$

Entropic pressure: multiplication of possibilities helps climb high mountains





$$V_{eff} = V(r) - T(d-1)\ln r$$

We may frame the discussion in terms of well-defined, measurable quantities

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Order appears as a logical consequence of super-Arrhenius timescales