Equation of State of a Model Glass

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Work with
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Related earlier work with

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Outline

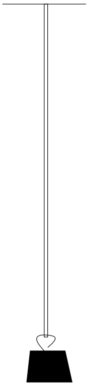
1. Introduction
2. Preliminaries
3. Definition of the model
4. Pico canonical Ensembles
5. Equation of state and entropy
6. Concluding remarks

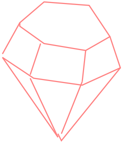
Equilibrium Statistical Mechanics

- System in thermal equilibrium
- Specify the N-particle hamiltonian $H = T + V$
- Calculate the partition function
  $\mathcal{Z}(N, V, T) = \prod_i \left[\int dp_i dq_i\right] \exp(-\beta H)$
- $F = -k_B T \log \mathcal{Z}$
  Pressure, energy etc. as derivatives of F
- $\langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}} \prod_i \left[\int dp_i dq_i\right] \exp(-\beta H)\, \mathcal{O}$
- Systematic approximation methods and variational principles

This prescription fails completely to describe a weight-supporting wire, or a diamond

$Prob(1gm.diamond) \sim \exp(-10^{22})$

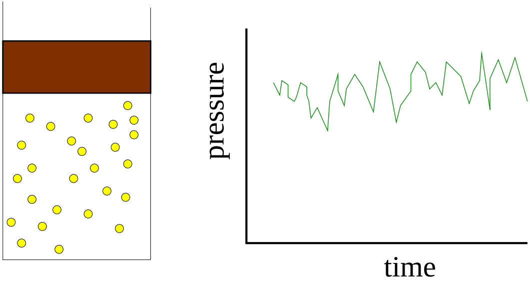




The Ergodicity Assumption

An isolated system, left to evolve, will visit all parts of constant energy surface.
No other constants of motion.

Time average in equilibrium = phase space average.



Only Effective ergodicity as Time required for sampling all phase space $\sim \exp(N)$

This ergodicy assumption NOT VALID for glasses/ diamonds.

"True long time averages" calculated correctly by equilibrium statistical mechanics.

Glasses and other metastable states

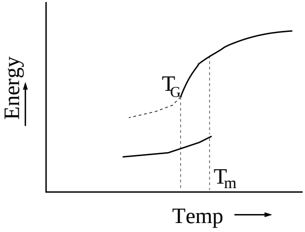
- Glasses usually treated as very slowly relaxing, non-equilibrium states of matter
- At laboratory time scales, Could matter such as window glass, or diamonds, be treated as in equilibrium?
  An equation of state?
- Will use “Glass" to refer to all broken-ergodicity states of matter.
  (supercooled liquids, solids with quenched disorder, allotrophes..)

Our Plan

- Treat glasses as states in Restricted equilibrium with Broken ergodicity.
  focus on long-time steady state properties
- Pico-canonical Ensembles
- Illustrative model with short-range interactions, Markov evolution, detailed balance, self-generated disorder
- Exact equation of state in a non-mean field model of glasses

Outline

A quick overview of phenomenology of glasses



- Most liquids, if rapidly cooled, fail to crystallize, and form an amorphous solid (glass).
- Below melting temperature, viscosity rises fast $\eta \sim \exp(+\frac{A}{T_* - T})$
- No latent heat, compressibility less in glass phase.
- strongly reduced Diffusion

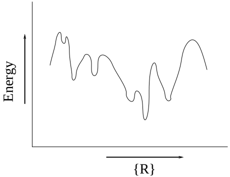
Theoretical Approaches to glasses

1.Mode-coupling theory

2.Inherent structures

Non-ergodic nature of glasses well recognized.

The energy landscape picture



Many local energy minima $\equiv$ inherent structures

Phase space decomposes into basins of attraction of different minima.

Only sum over states near one minima.

Number and volumes of basins very difficult to estimate.

estimated time spent in one minima in real glasses $\sim 10^{-10}$ sec.

Metabasins

3. Constrained Kinetics models (Ritort & Sollich 2003)

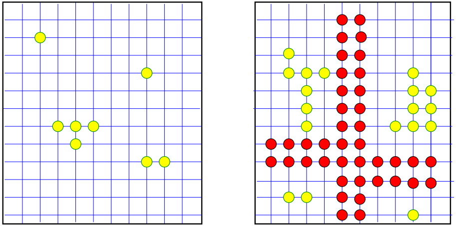
Markovian evolution, detailed balance, Broken ergodicity

Trivial Hamiltonian, Usually focus on slow relaxation.

Hard-core lattice gas models

Particles can hop to nearest neighbor iff neither initial or final site of step has more than 2 occupied neighbors.

At low densities particles diffuse all over lattice.
At higher density, some particles are fully immobile.
Others can only rattle in cages.



Jamming

Outline

Restricted thermal equilibrium

“If a system is weakly coupled to the heat bath at a given ‘temperature’, if the coupling is indefinite, and not known precisely, if the coupling has been on for a long time, and if all the ’fast’ things have happened, and all the ’slow’ things not, the system is said to be in thermal equilibrium".

R. P. Feynman, Statistical Mechanics

To define equilibrium, **we have to set the rate of slow processes to zero.**

e.g hydrogen gas at room temp, iron rod in thermal equilibrium in air.

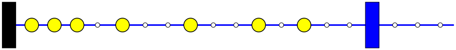
The Model

One dimensional lattice gas of N particles

Piston on right end.

$$H = -J \sum_i n_i n_{i+1} + pX_P$$

Interaction with piston and left wall also $-J$



Markovian continuous time evolution.

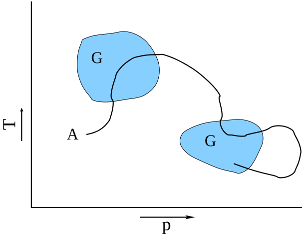
one-step jump $01 \rightleftharpoons 10$, rate $\Gamma_1 \exp(-\beta \Delta E/2)$.

two-step jump $100 \rightleftharpoons 001$, rate $\Gamma_2 \exp(-\beta \Delta E/2)$.

piston move $0P \rightleftharpoons P0$, rate $\Gamma_3 \exp(-\beta \Delta E/2)$.

Rates satisfy detailed balance.

Assume that $\Gamma_1(p, T)$ is zero in some regimes.
Γ_2, Γ_3 always nonzero.



- If $\Gamma_1 \neq 0$,steady state is the canonical Boltzmann-Gibs distribution
  $\mathrm{Prob}(C) = (1/\mathcal{Z})\exp[-\beta H(C)]$
- If $\Gamma_1(p, T) = 0$, then dynamics is not ergodic.

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Pico canonical Ensembles

- In non-glassy regions, unique equilibrium state for each (p, T)
- Entering a glassy region, system falls in one of the sectors
  $Prob(S) = \mathcal{Z}_S(p, T)/\mathcal{Z}(p, T)$
  $\mathcal{Z}_S$ is the pico-canonical partition function.

$$\mathcal{Z}_S(p, T) = \sum_{C \in S} e^{-\beta H(C)}$$

- As we vary (p, T) within a glassy region, sector does not change
- $Prob(S)$ depends only on point of entering glassy region

Pico canonical Ensembles

- Average in a sector by usual method e.g.$\langle L \rangle_S \quad = \quad k_B T \frac{\partial}{\partial p} \log \mathcal{Z}_S$
- Finally, $\quad \langle O \rangle = \sum_S Prob(S) \langle O \rangle_S$
- self-generated quenched disorder

This prescription is usually rather difficult to implement explicitly, but this can be done exactly in our simple model.

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Define $\Delta_i = x_{i+1} - x_i$
then
$H = \sum_i [-J\delta_{\Delta_i,1} + p\Delta_i]$
Hence in the ergodic phase, the partition function is
$\mathcal{Z} = w(u,x)^{N+1}$
where $w = ux + x^2 + x^3 + x^4$..
and $u = \exp(\beta J), x = \exp(-\beta p)$.

Mean spacing between particles = $x\frac{\partial}{\partial x}\log\mathcal{Z}(u,x)$

Equation of state in the high density phase (Takahashi, 1942).

In the Glass phase,

$\eta_i = \Delta_i (mod 2) \;\; i = 1 \; to \; N$ conserved by dynamics.

2^N disjoint sectors.

Within a sector, relative probabilities are Boltzmann-Gibbs.

$$Prob(C|S) = \frac{1}{\mathcal{Z}_S} \exp(-\beta H(C))$$

$$\mathcal{Z}_S = w_{odd}^R w_{even}^{N-R} w$$

where R is the number of odd η's.

and

$$w_{odd} = ux + x^3 + x^5 + x^7 + \ldots$$

$$w_{even} = x^2 + x^4 + x^6 + \ldots$$

Equation of state and entropy

If we enter the glass phase at point (u^*, x^*)

Define

$\alpha^* = w_{odd}(u^*, x^*)/w(u^*, x^*)$

Then

$Prob(S) = \alpha^R (1 - \alpha^*)^{N-R}$

Straightforward calculation gives

$\langle \Delta \rangle = \alpha^* \langle \Delta \rangle_{odd} + (1 - \alpha^*) \langle \Delta \rangle_{even}$

This gives the density in the glassy phase.

Mean energy calculation similar.

Equation of state and entropy

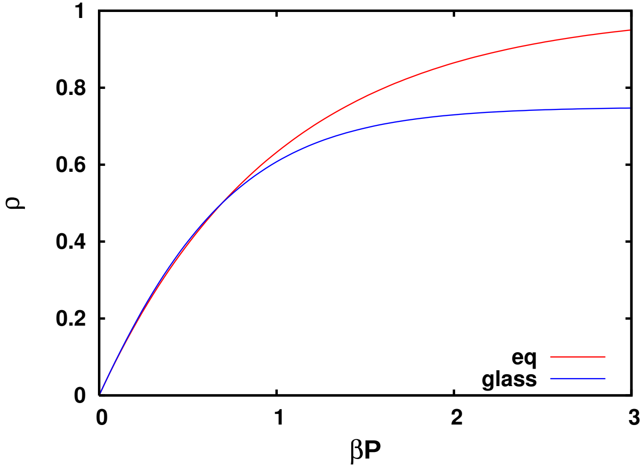


Figure: Plot of density as a function of presssure for $J = 0$, $x^* = 1/2$

Equation of state and entropy

Boltzmann's formula; $S = k \log \Omega$
Is there a change in entropy across the glass transition?

In general, $E = \sum_i p_i E_i$
Hence, $\Delta E = \sum_i [p_i \Delta E_i \ + \ E_i \Delta p_i]$

$$= \Delta W + \Delta Q$$

In our model both are zero. No latent heat.

Equation of state and entropy

$$S_{total} = S_{frozen} + \langle S_{pico} \rangle_{\mathbb{S}}$$

where

$$S_{frozen} = -\sum_{sectors} \mathrm{Prob}(\mathbb{S}) \log \mathrm{Prob}(\mathbb{S})$$

and

$$S_{pico}(\mathbb{S}) = -\sum_{C \in \mathbb{S}} \mathrm{Prob}(C|\mathbb{S}) \log \mathrm{Prob}(C|\mathbb{S})$$

The frozen entropy is real.

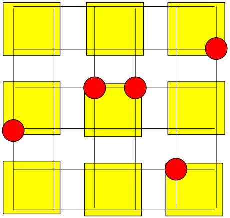
Outline

Generalizations:

1: next neighbor couplings,

2: step size 3, instead of 2, ...

3: Higher dimensions:



Exact calculation difficult.

Relation to the earlier studied DRD model

Model of Diffusing Reconstituting Dimers

$$01 \rightleftharpoons 10$$
$$011 \rightleftharpoons 110$$

Similar sector decomposition, but no satisfactory definition of pressure.

e.g. consider $0010110000110010P00$

The glass phase is incompressible.

No equation of state.

Concluding remarks

- In our model, the state in the glassy phase depends only on (p, T) and (u^*, x^*).

  More generally, a sequence of ergodicity breaking transitions.
  Then, more complicated history dependence $(u_1^*, x_1^*)(u_2^*, x_2^*), \ldots$.

Thank You.

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