Kinetically constrained models and dynamical facilitation

Lecture 1 – Kinetically constrained models (KCMs)

Lecture 2 – Dynamical facilitation:
KCMs as ‘realistic’ models

Are KCMs like real glasses?

In favour

- Fluid states with slow, co-operative, heterogeneous dynamics

Against

- No elasticity, phonons, β-relaxation
- Simple thermodynamic properties (but this might also be an advantage)

Recall:
Probabilities of specific configurations are the same for different KCMs.
. . . but probabilities of trajectories are different

A purely dynamic glass transition

Freezing: liquid $\rightarrow$ crystal:

Probabilities of configurations change qualitatively.

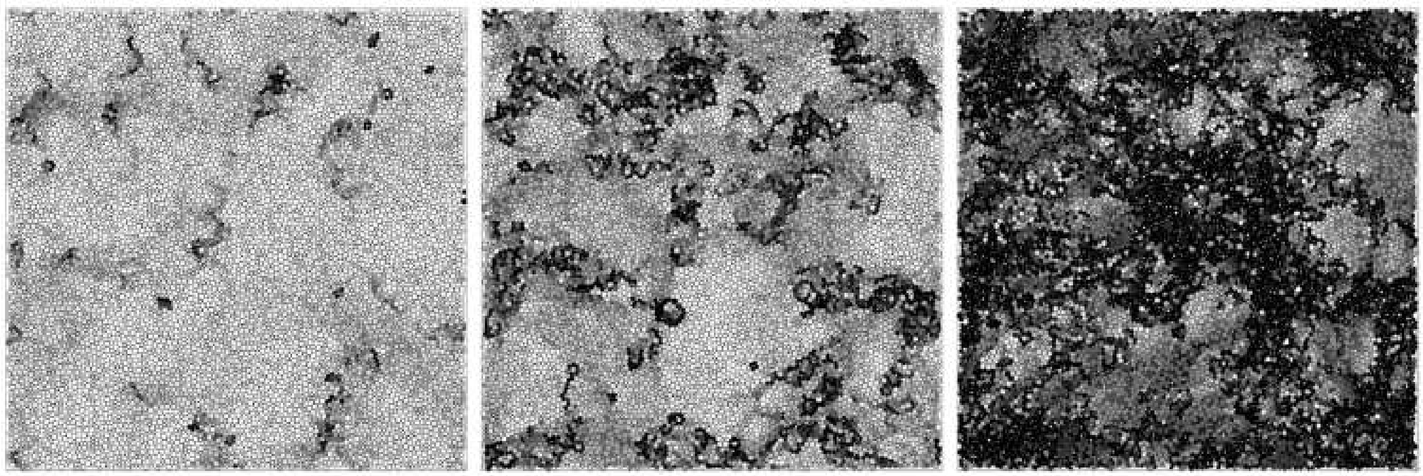
Compare: liquid $\rightarrow$ glass:

Probabilities of configurations change only slightly

Probabilities of trajectories change qualitatively.

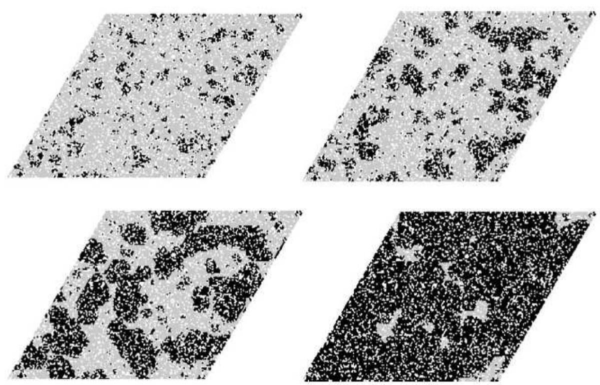
Motivation: whereever possible, ignore configurational quantities including liquid structure, entropy; focus on dynamical quantities such as relaxation time and heterogeneity.

Facilitation



$2d$ mixture of repulsive particles [Garrahan and Chandler, 2009]
(molecular dynamics, not a KCM)
Time increases from left to right. Darker particles have moved further.

Observe 'spreading of mobility':
[Pan, Garrahan and Chandler (2005)]



KCMs and facilitation

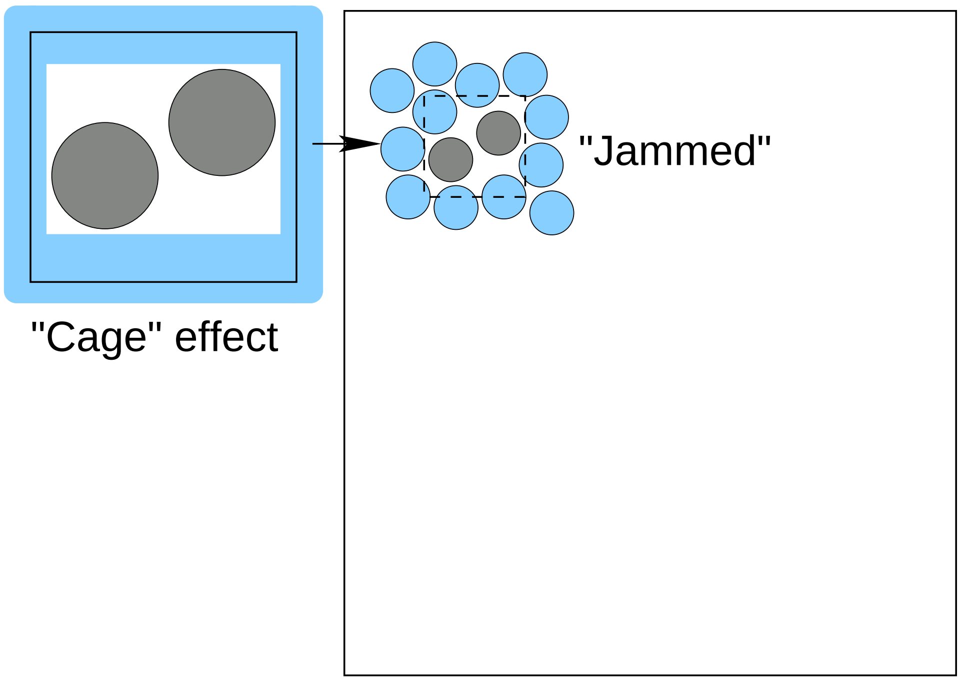
In using a KCM to describe a realistic system, we somehow assume that facilitation is the dominant effect.

Analogy: if gas particles attract each other, they tend to make liquids (or sometimes crystals).
Can use simple models (eg Ising) to descripe condensation: these models contain only a few ingredients of the system but still describe it semi-quantitatively.

Many people agree that facilitation exists in glassy liquids.
The question of its dominance is much more controversial.
Idea of this dominance proposed by Garrahan & Chandler.

One hypothesis : all ‘interesting’ features of glassy liquids can be explained in terms of KCMs.

Coarse-graining



System may be local jammed or mobile.

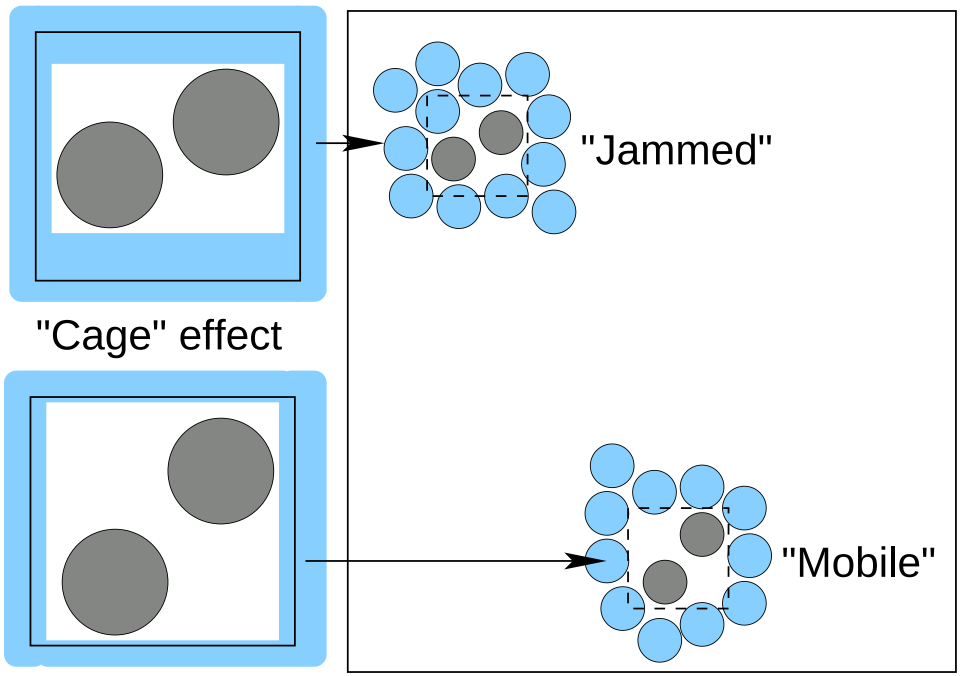
Like an FA model with jammed being $n_i = 0$, and mobile being $n_i = 1$.

Regions tend to become mobile only when nearby regions are mobile (that is the idea of facilitation)

Think in terms of a ‘mapping’ from the liquid to the KCM [Garrahan and Chandler, (2003)]

(neglect of elasticity might be important here)

Coarse-graining



System may be local jammed or mobile.

Like an FA model with jammed being $n_i = 0$, and mobile being $n_i = 1$.

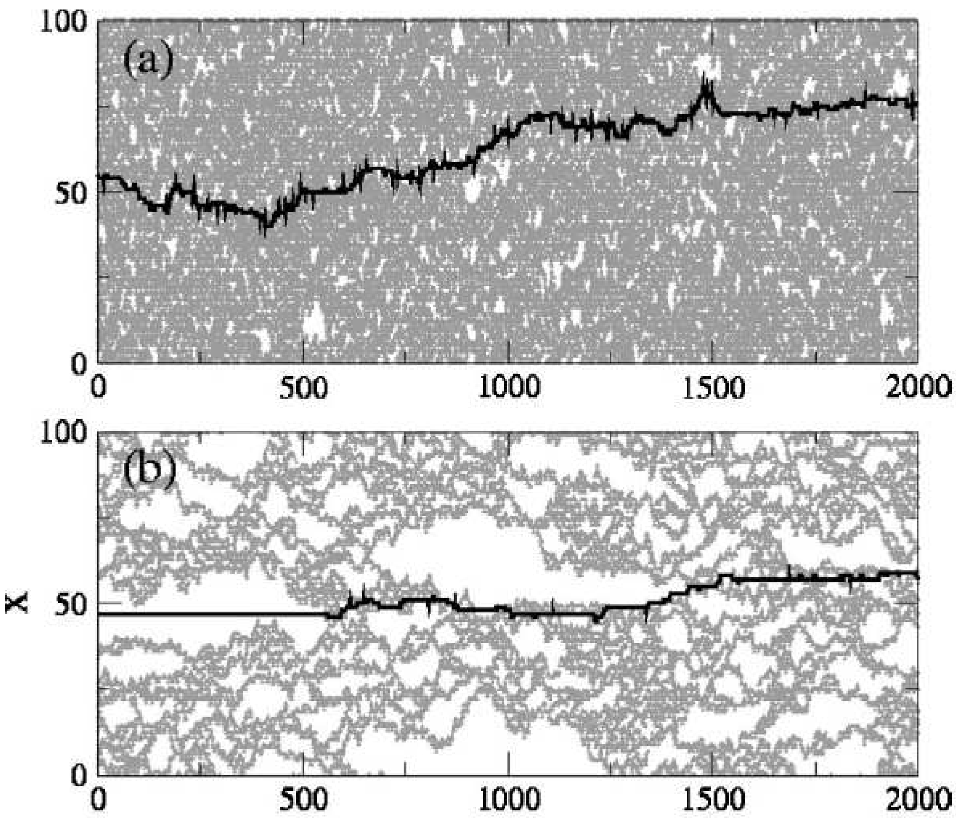
Regions tend to become mobile only when nearby regions are mobile (that is the idea of facilitation)

Think in terms of a 'mapping' from the liquid to the KCM [Garrahan and Chandler, (2003)]

(neglect of elasticity might be important here)

Single-particle picture

We want to consider motion of a particle in this fluctuating environment. Suppose that the n_i evolve independently of the particle, but the particle can hop only between sites with $n_i = 1$.



1-FA for example

Grey : $n_i = 1$;
white $n_i = 0$;
Black : single particle

Particle motion is intermittent when c is small.

[Jung, Garrahan and Chandler (2004)]

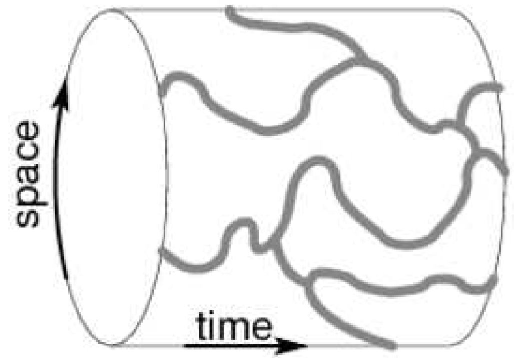
Stretched exponential relaxation

In supercooled liquids, often fit $F_\mathrm{s}(k,t) \approx q\exp(-(t/\tau_\alpha)^\beta)$ for structural relaxation ($t \approx \tau_\alpha$), $\beta < 1$.

1-spin facilitated FA:

Excitation density c.

Diffusion constant for *excitations* is $D \sim c$



Particle is a distance ℓ from the nearest excitation.
It moves for the first time at $t \sim \ell^2/D$.

Fraction of particles that are distance $\ell > x$ from nearest excitation: e^{-cx},
Fraction that have not moved at all at time t: $P(t) \sim \mathrm{e}^{-c\sqrt{Dt}}$
(stretching, $\beta = 0.5$, $\tau \sim c^{-3}$)

Stretched exponentials (2)

Working more carefully, can check that

- $F_{\rm s}(k,t)$ for probe particles does follow $\mathrm{e}^{-A\sqrt{c^3 t}}$ for $t \approx t_\alpha$.
- Proven crossover to exponential at longer times.
  (but stretched exponential is just a fit)
- FA with $f = 1$ has simple exponential in $d \geq 2$.
- Other KCMs have various $\beta < 1$.

Conclusion: in KCMs, stretched exponentials arise from a distribution of particle environments (near and far from excitations).

Stretching linked to dynamical heterogeneity.

Stokes-Einstein relation

In simple liquids (high temperatures), general arguments imply

$$\eta \sim \tau \sim D_{\rm p}^{-1}$$

(viscosity η, relaxation time τ, diffusion constant $D_{\rm p}$)

Observed to break down in supercooled regime.

Tentative explanation: there is a range of relaxation times τ, depending on local environments (ie heterogeneity again)

Can we test this idea in KCMs?

We have a lattice, so particles move in discrete hops. Consider a ‘jump model’, using *continuous time random walk*.

Jump models, CTRW

Particle on a lattice, moving by unbiased hops.
Times between hops are independent random variables with distribution $\psi(t)$. [Berthier lectures]

A surprising(?) thing about probabilities:

Mean exchange time τ_x: the average time between successive hops.

Mean persistence time τ_p: starting at a random time, the average time before the next hop takes place

Can (easily) show that

$$\tau_\mathrm{x} = \int \mathrm{d}t\, t\psi(t)$$

$$\tau_\mathrm{p} = \tau_\mathrm{x}^{-1} \int \mathrm{d}t\, t^2\psi(t)$$

The persistence time notices the large times more. . .

CTRW and decoupling

Within CTRW, we have

Particle diffusion constant $D_\mathrm{p} = a^2/\tau_\mathrm{x}$

Structural relaxation time is $\tau_\alpha \simeq \tau_\mathrm{p}$.

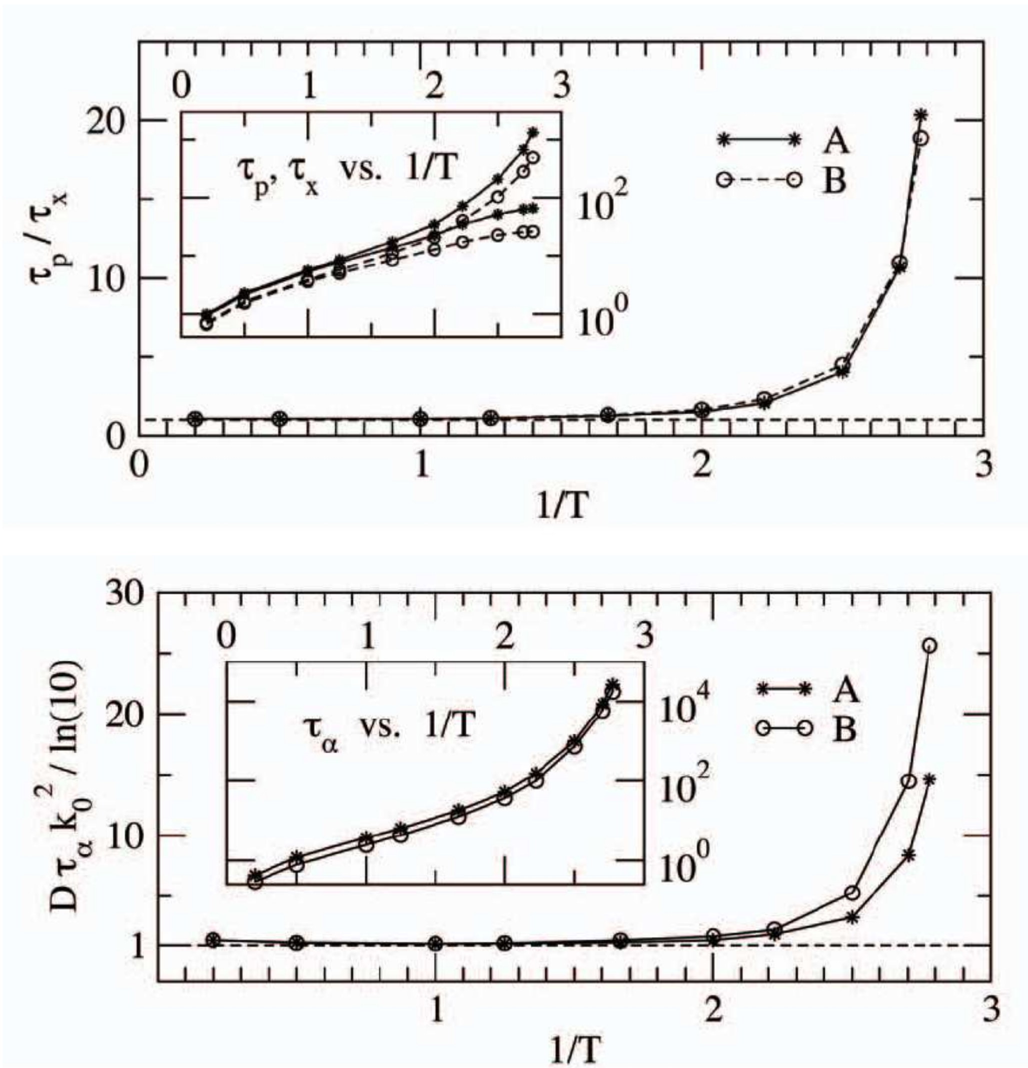
If particles follow CTRW, expect

$$D_\mathrm{p}\tau_\alpha \approx a^2(\tau_\mathrm{p}/\tau_\mathrm{x})$$

This is

- Good for 1-FA (in $1d$)
- Bad for East and other models
  Hop directions are not independent: more likely to go back than twice in the same direction
- Extend idea to real liquids…

Exchange, persistence and decoupling



$2d$ mixture of repulsive particles

Top : ratio of persistence and exchange times

Bottom : $D_{\mathrm{p}}\tau_{\alpha}$.

Semi-quantitative agreement with CTRW theory

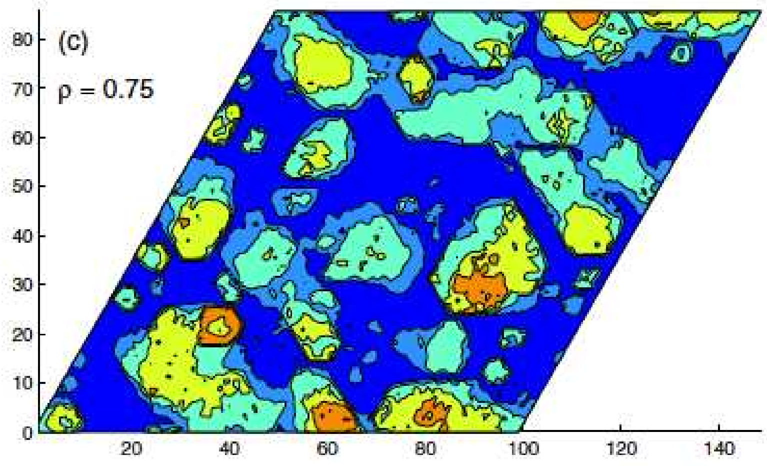
[Hedges, Maibaum et al (2007)]

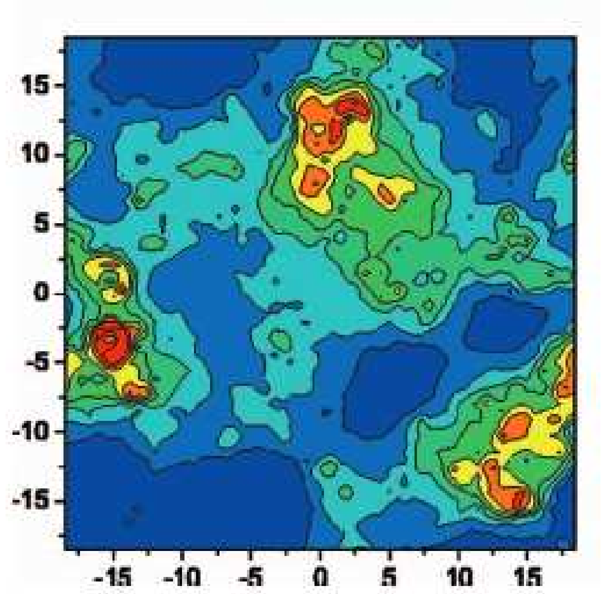
Note : Facilitation enters only *indirectly*, through $\psi(t)$.

Collective behaviour

Should also consider correlations between particles.

Dynamical propensity: for a typical configuration, measure averaged displacements for each particle in time τ_α





Left: TLG model. [Hedges and Garrahan (2007)];
Right: repulsive particles. [Widmer-Cooper & Harrowell, (2007)]
Bright colours show mobile particles, clustered in space.

KCMs show similar phenomena to simulated glass-formers.

What about Vogel-Fulcher?

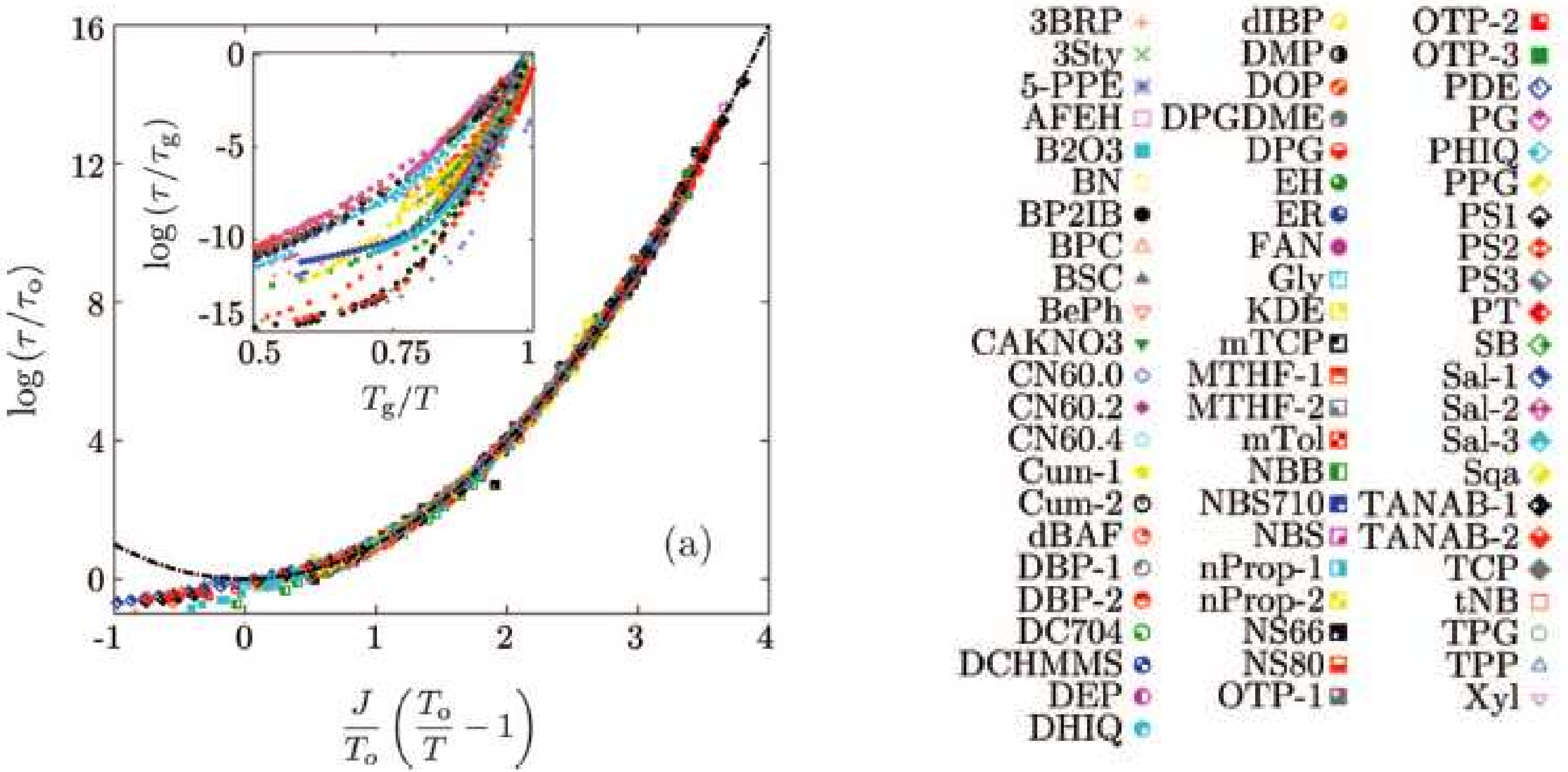
Often, glassy liquid data is fitted to $\tau \sim \mathrm{e}^{A/(T-T_{\mathrm{K}})}$

For consistency with KCMs, try instead $\tau \sim \mathrm{e}^{A/T+B/T^2}$

What about Vogel-Fulcher?

Often, glassy liquid data is fitted to $\tau \sim \mathrm{e}^{A/(T-T_{\mathrm{K}})}$

For consistency with KCMs, try instead $\tau \sim \mathrm{e}^{A/T+B/T^2}$



VTF not necessary [Elmatad, Garrahan and Chandler (2009)]

So what?

What can we conclude thus far?

- Models with simple thermodynamic properties can still be ‘glassy’.

- Can get a long way without asking about liquid structure.
  (We ask where mobility happens, but we don’t attempt to associate it with structural features.)

So what?

What can we conclude thus far?

- Models with simple thermodynamic properties can still be ‘glassy’.

- Can get a long way without asking about liquid structure.
  (We ask where mobility happens, but we don’t attempt to associate it with structural features.)

What would qualify as a ‘working theory of the glass transition’?

– Machinery for exact analytic calculations on liquids?

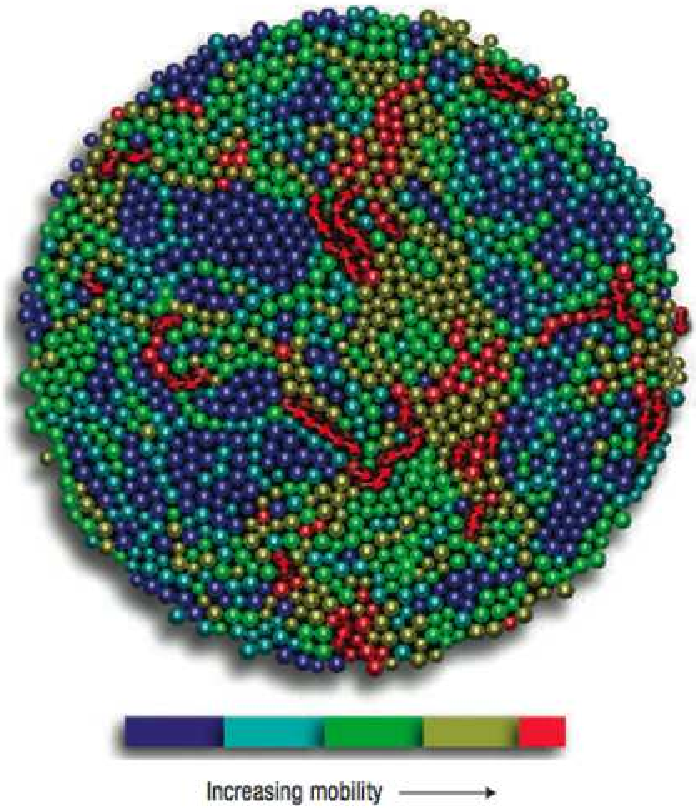
– Precise procedure for mapping liquids $\leftrightarrow$ KCMs?

– ‘Universal’ features of KCMs revealed in liquids?

Facilitation in granular media

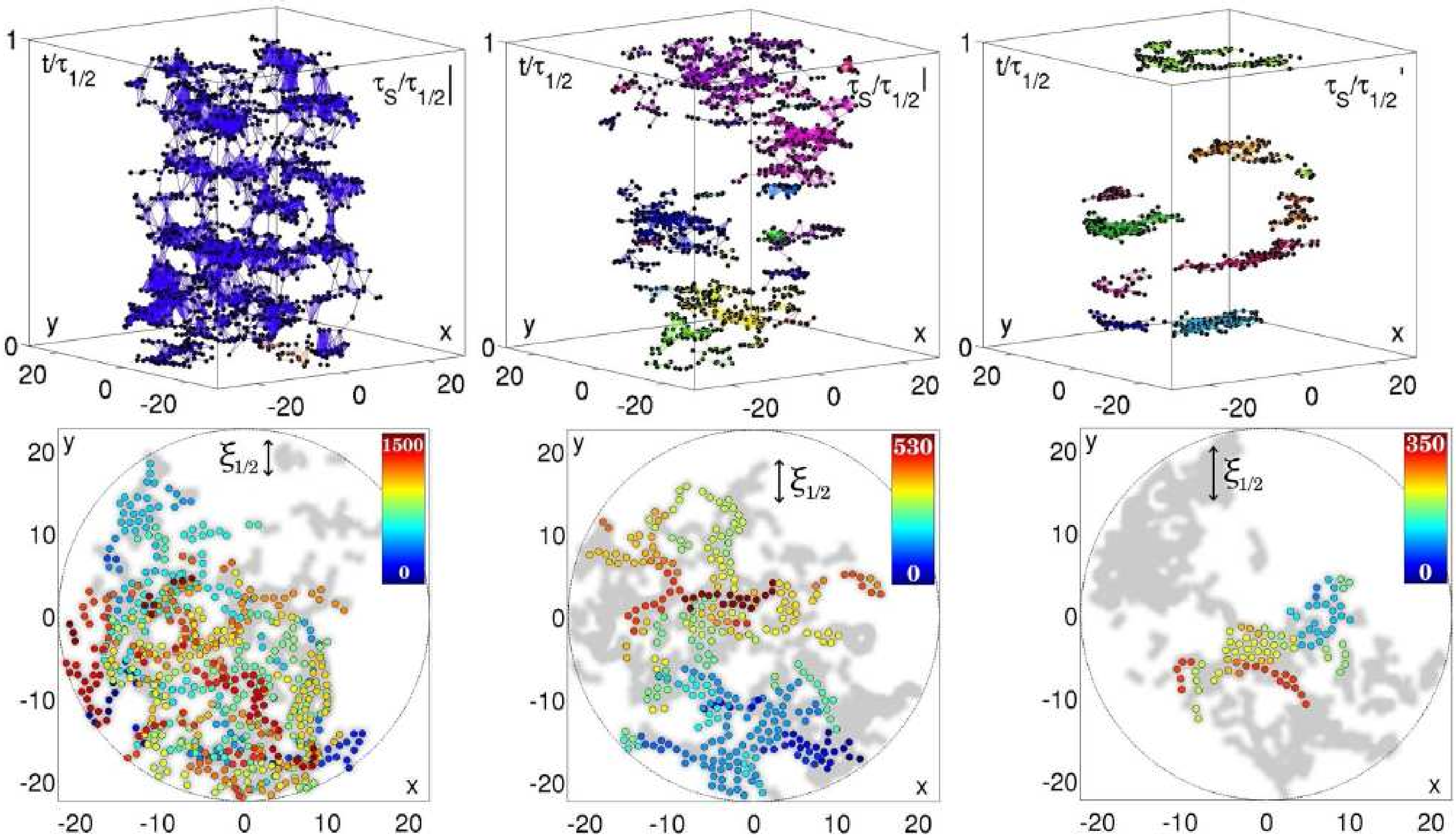
Take ball-bearings in $2d$ in a vertical air current.

At high density, see ‘glassy’ heterogeneous dynamics.



[Keys et al (2007)]

Direct evidence for facilitation



Mobile clusters in space and in space-time, as density is increased [Candelier, Dauchot and Biroli (2009)]

Mapping to KCM

Facilitation is a strong effect, at least in granular ‘glasses’.

Can we map to excitations with local rules?

Difficult

- Sometimes observe motion starting far from excitations
- Difficult to associate excitations with structural feature (Is this a problem?)
- Expect facilitation to be a stronger effect at low temperature and high density: can this scaling be found?

. . . work continues in this area

A new idea. . .

. . . about universal glassy physics.

Most KCMs remain ergodic at all temperatures/densities.
No ‘ideal glass transitions’ in these models

Idea: to find a phase transition, extend the methods of thermodynamics from space to space-time.

Eg, in microcanonical ensemble in stat mech:
– Consider configurations with fixed energy E.

Now we consider instead
– trajectories with a fixed value of an activity K, which is the number of accepted moves in a trajectory of length t_{obs}.

. . . or equivalent ‘canonical ensemble’:
– use a biasing field s analogous to the temperature, which fixes $\langle K \rangle$ instead of K itself.

Thermodynamics, and trajectories

[Ruelle, Gallavotti-Cohen, Lebowitz-Spohn, Gaspard, Maes, many others]

Statistics of configurations

$$Z(\beta) = \sum_{\text{conf}} e^{-\beta E_{\text{conf}}}$$

Change pressure by Δp,
conjugate to V

$$Z(\beta, \Delta p) = \sum_{\text{conf}} e^{-\beta E_{\text{conf}}} e^{-\Delta p \beta V_{\text{conf}}}$$

$$\langle V \rangle_p = \frac{\partial}{\beta \partial \Delta p} \log Z(\beta, \Delta p)$$

Thermodynamics, and trajectories

[Ruelle, Gallavotti-Cohen, Lebowitz-Spohn, Gaspard, Maes, many others]

Statistics of configurations

$$Z(\beta) = \sum_{\text{conf}} e^{-\beta E_{\text{conf}}}$$

Statistics of trajectories

$$\mathcal{Z} = \sum_{\text{traj}} P_{\text{traj}}$$

Change pressure by Δp, conjugate to V

$$Z(\beta, \Delta p) = \sum_{\text{conf}} e^{-\beta E_{\text{conf}}} e^{-\Delta p \beta V_{\text{conf}}}$$

$$\langle V \rangle_p = \frac{\partial}{\beta \partial \Delta p} \log Z(\beta, \Delta p)$$

Thermodynamics, and trajectories

[Ruelle, Gallavotti-Cohen, Lebowitz-Spohn, Gaspard, Maes, many others]

Statistics of configurations

$$Z(\beta) = \sum_{\text{conf}} e^{-\beta E_{\text{conf}}}$$

Change pressure by Δp, conjugate to V

$$Z(\beta, \Delta p) = \sum_{\text{conf}} e^{-\beta E_{\text{conf}}} e^{-\Delta p \beta V_{\text{conf}}}$$

$$\langle V \rangle_p = \frac{\partial}{\beta \partial \Delta p} \log Z(\beta, \Delta p)$$

Statistics of trajectories

$$\mathcal{Z} = \sum_{\text{traj}} P_{\text{traj}}$$

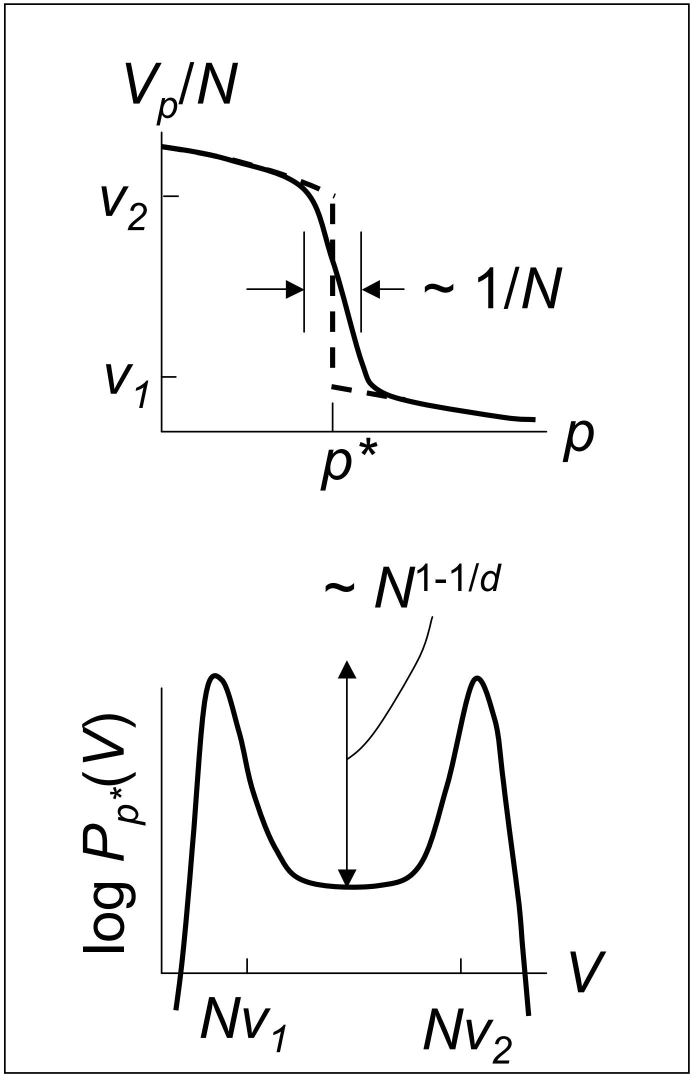
Order parameter: mobility K

$$\mathcal{Z}(s) = \sum_{\text{traj}} P_{\text{traj}} e^{-s K_{\text{traj}}}$$

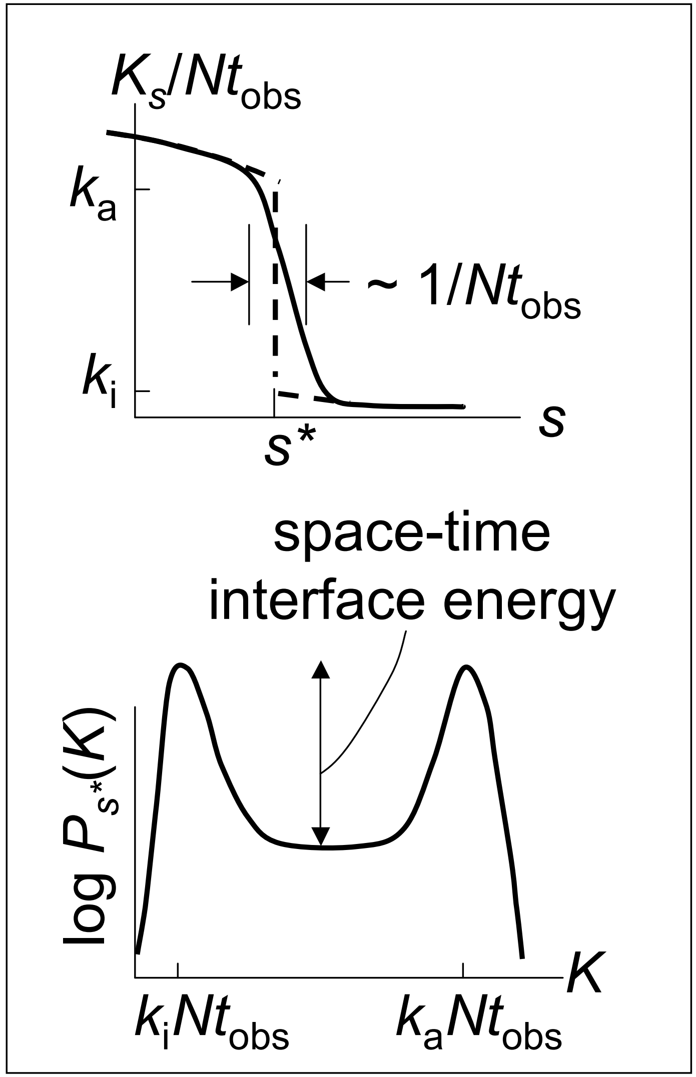
$$\langle K \rangle_s = -\frac{\partial}{\partial s} \log \mathcal{Z}(s)$$

First-order phase transitions

Equilibrium

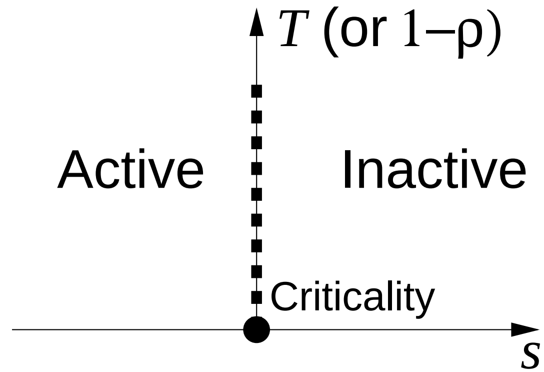


Non-equilibrium

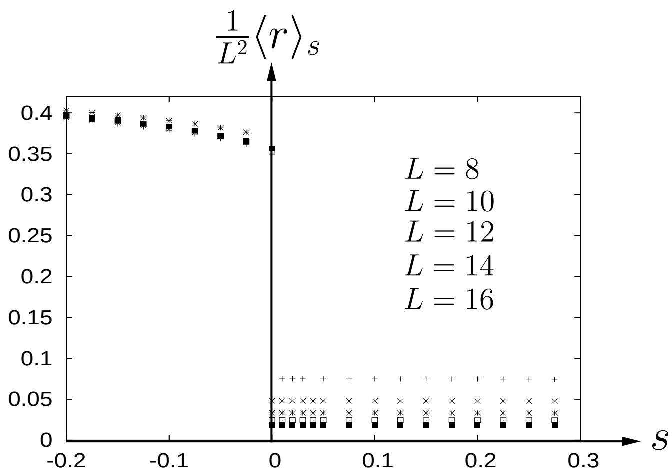


KCM : results

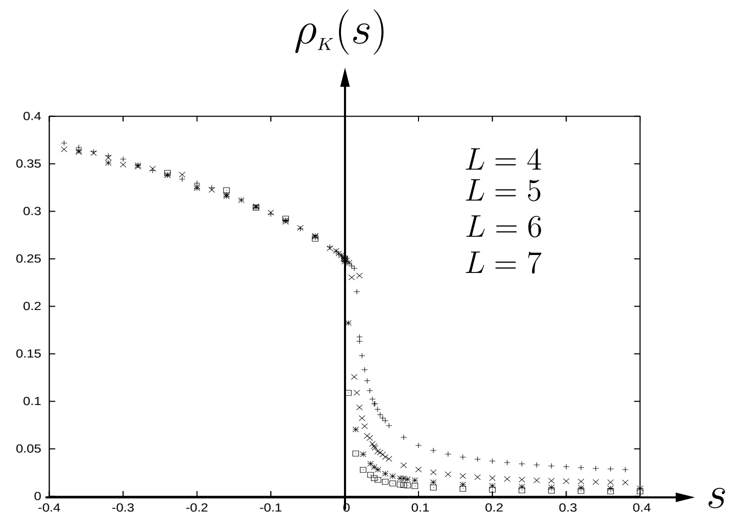
Analytic:
Presence of any ‘inactive’ configuration
$\Rightarrow$ first-order transition at $s = 0$.



Numerical: (cloning, $t_{\mathrm{obs}} \to \infty$, vary L)



(TLG model, $d = 2$)



(East model, $d = 3$)

[Garrahan et al (2007)]

Is this an artefact of KCMs?

Repeat similar analysis in system of Lennard-Jones particles…

Activity K becomes indicator of local motion:

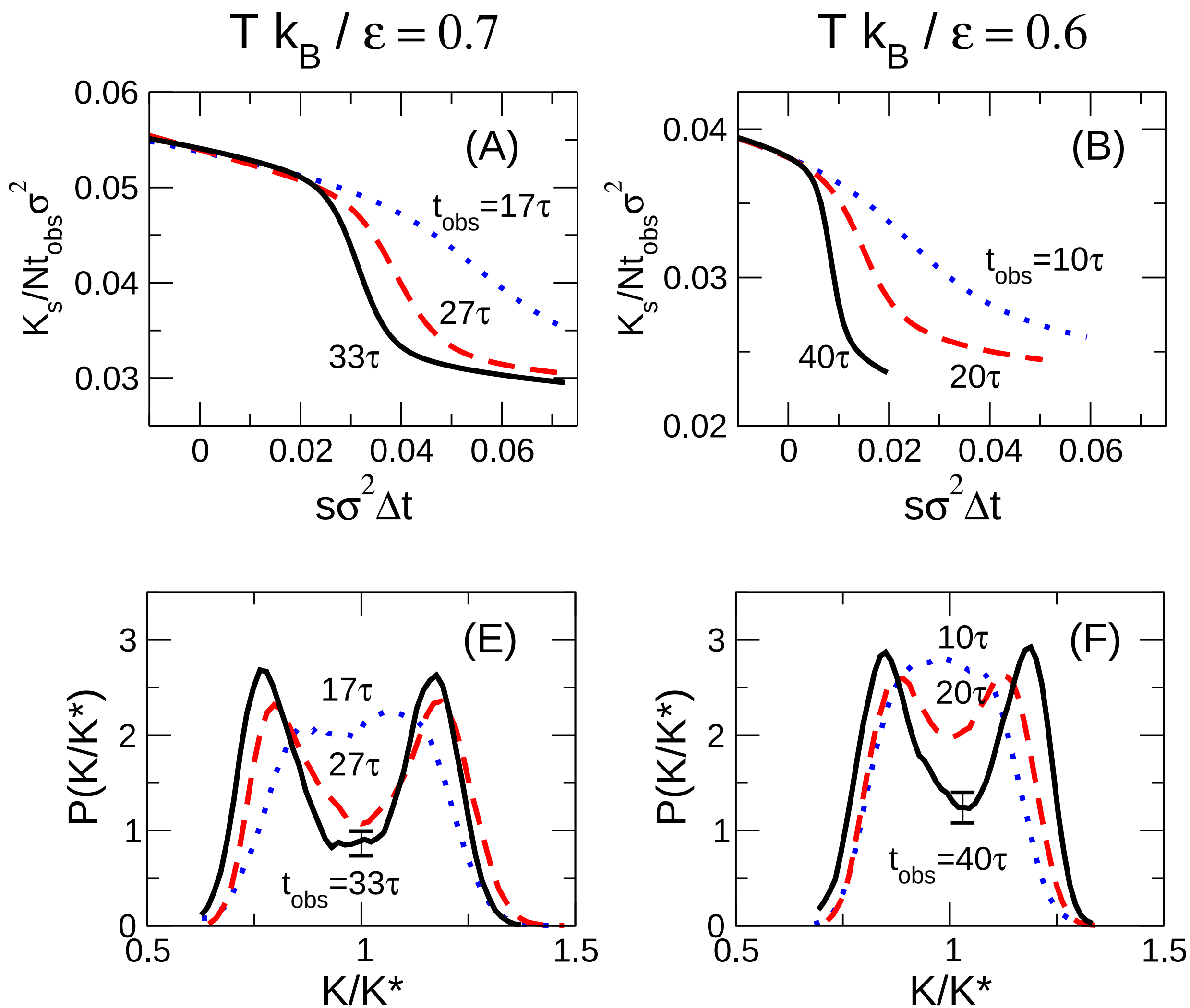
$$K = \sum_{it} |\boldsymbol{r}_i(t + \Delta t) - \boldsymbol{r}_i(t)|^2$$

$\boldsymbol{r}_i(t)$: position of particle i at time t.

Sum over t runs over equally-spaced times.

…computer simulations…

LJ system : results



Evidence for first-order transition in atomistic system

Value of s^* is small but non-zero

Transition to a 'glassy' phase

[Hedges et al (2009)]

Conclusions

- Dynamical faciliation is the idea that particle motion tends to occur in regions of space near to previously mobile regions.
- This idea is encapsulated in KCMs, and observed in experiments
- KCMs can be useful as simple model systems in which to test the relationships between phenomena like dynamical heterogeneity, stretched exponential relaxation and Stokes-Einstein decoupling.
- The kinds of arguments used in these lectures have emphasised that these dynamical phenomena can be explained without reference to structural or thermodynamic ideas.