Dynamical heterogeneity in thin polymeric films: the least mobile clusters and their possible role in the glass transition

Arlette Baljon, Joris Billen, *San Diego State University*
Regina Barber-DeGraaff, *Washington State*
Rajesh Khare, *Texas Tech*

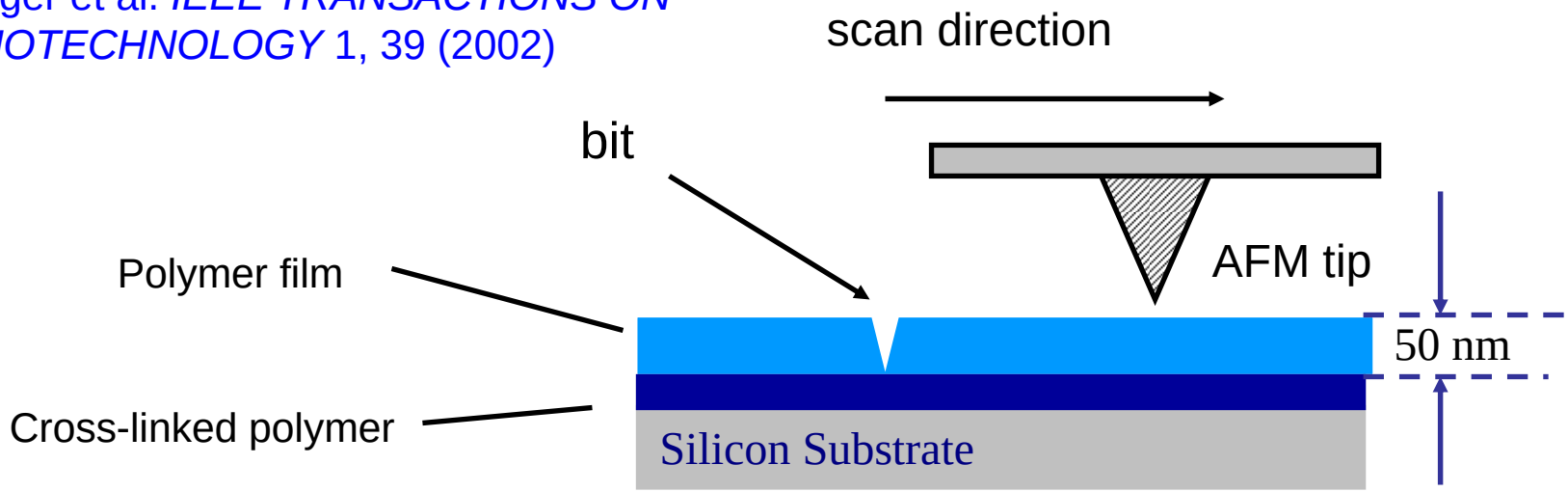
Outline:

- Introduction
- Model
- Determination of transition temperatures
- Percolation of clusters of slow dynamics
- Recent work by other groups

PRL **93**, 255701 (2004), Macromolecules **38**, 2391 (2005)

Millipede Data Storage Technology

Vettiger et al. *IEEE TRANSACTIONS ON NANOTECHNOLOGY* 1, 39 (2002)



- **Thermomechanical read/write process in nanoscale polymer films using AFM-like tip**
- **A "bit" is written by heating the polymer film above its glass transition temperature and then creating an indentation in it using an AFM-like tip**
- **Polymer film used should be easily deformable for bit writing, written bits should be stable and it should be possible to repeatedly erase and rewrite the bits**

Glass Transition Behavior of Thin Films

Decrease in T_g of thin polymer films compared to bulk value:

- **Free standing films**
- **Forrest et al. (1997): Decrease of glass transition temperature with film thickness of up to 60 deg.**
- $T_g(h) = T_g^{bulk}\left(1 - \frac{h_0 - h}{\zeta}\right)^{1.8}$ for low M_W.

  chain length dependence for high M_W.

Increase in T_g of thin polymer films compared to bulk value:

- **Supported films with absorbing substrate**
- **Fryer et al. (2001): Tuning the interfacial energy raises the T_g of PS films by about 10-15 deg above the bulk value.**
- **Tate et al. (2001):**

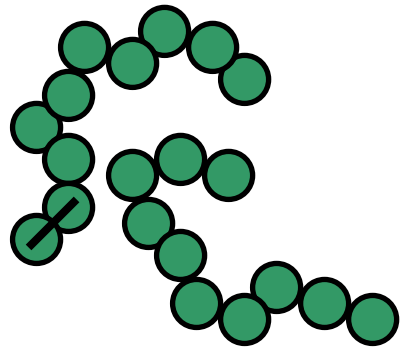
  Chain grafting to the substrate has a significant effect on the T_g (up to 55 deg increase)

Model System

- **Bead-spring model (Kremer/Grest):**

  Polymer: Bead-spring chain

  40 chains, chain length = 100



Lennard-Jones Potential

$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Anharmonic Spring

$$V_S(r) = 0.5kR_o^{\,2}\ln[1-(\frac{r}{R_o})]$$

All quantities are reported in reduced Lennard-Jones units

$\sigma \approx 0.5nm$ $\varepsilon \approx 30meV$ $\tau \approx 5ns$

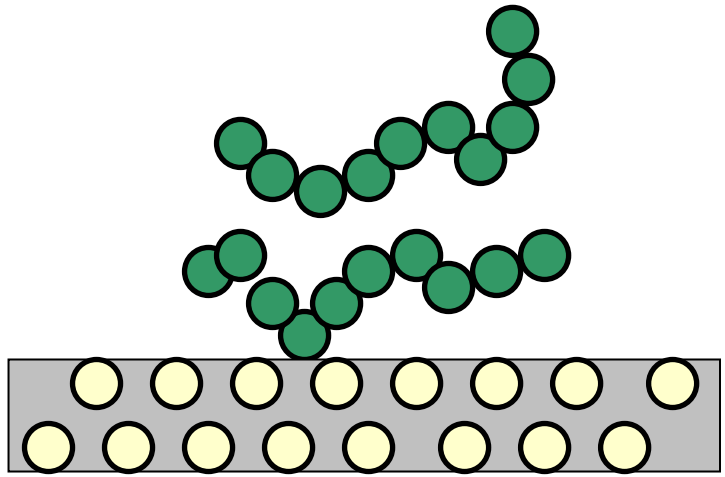
Model System contd.

- **Substrate: atoms on a lattice**

  Lennard-Jones interactions between the chain beads and surface beads

  $\sigma_{ps} = 0.9\,\sigma$

  $\varepsilon_{ps} = \varepsilon$

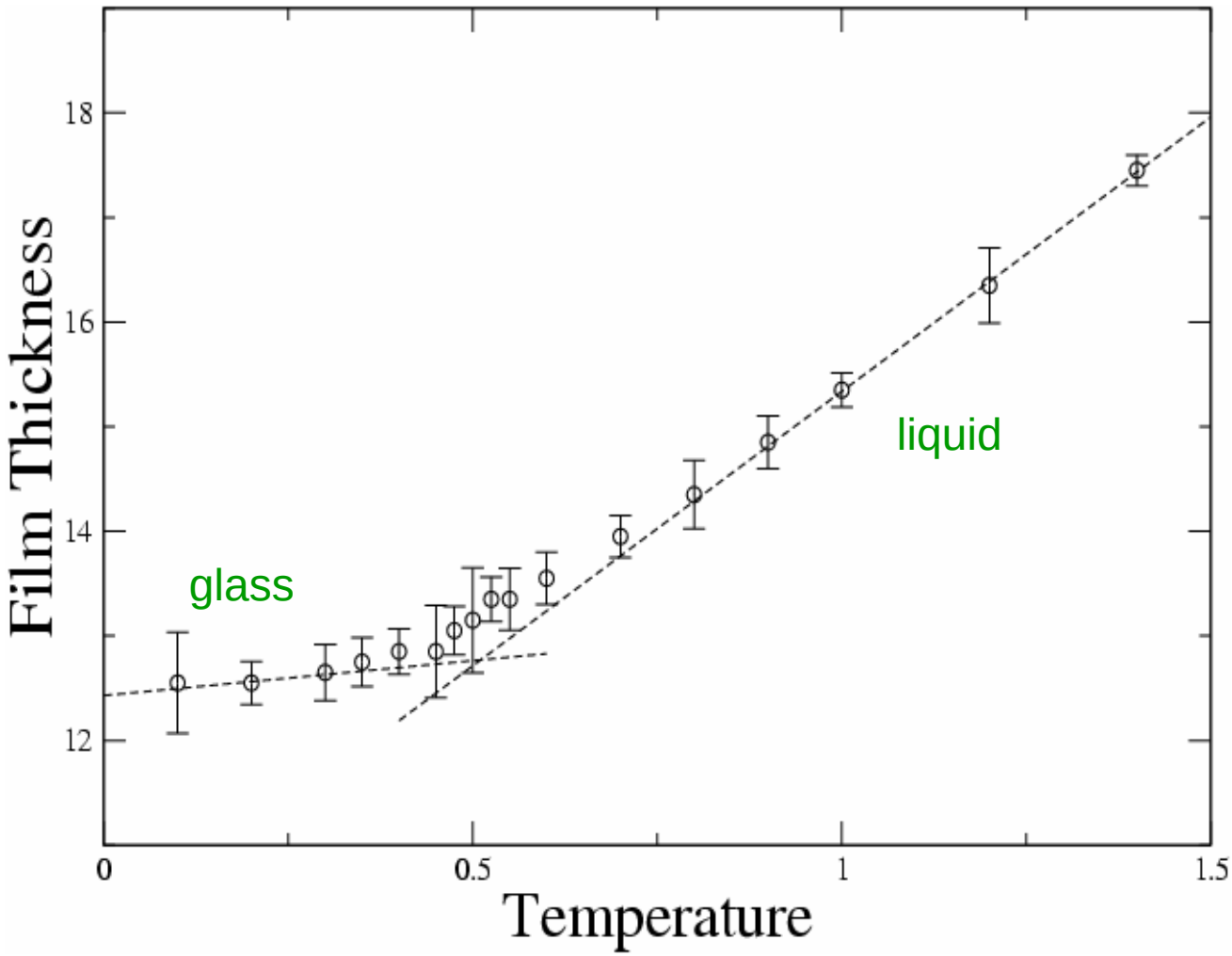


Supported film
Absorbing substrate

- **Molecular dynamics simulations at constant temperature**

3D
Periodic boundaries

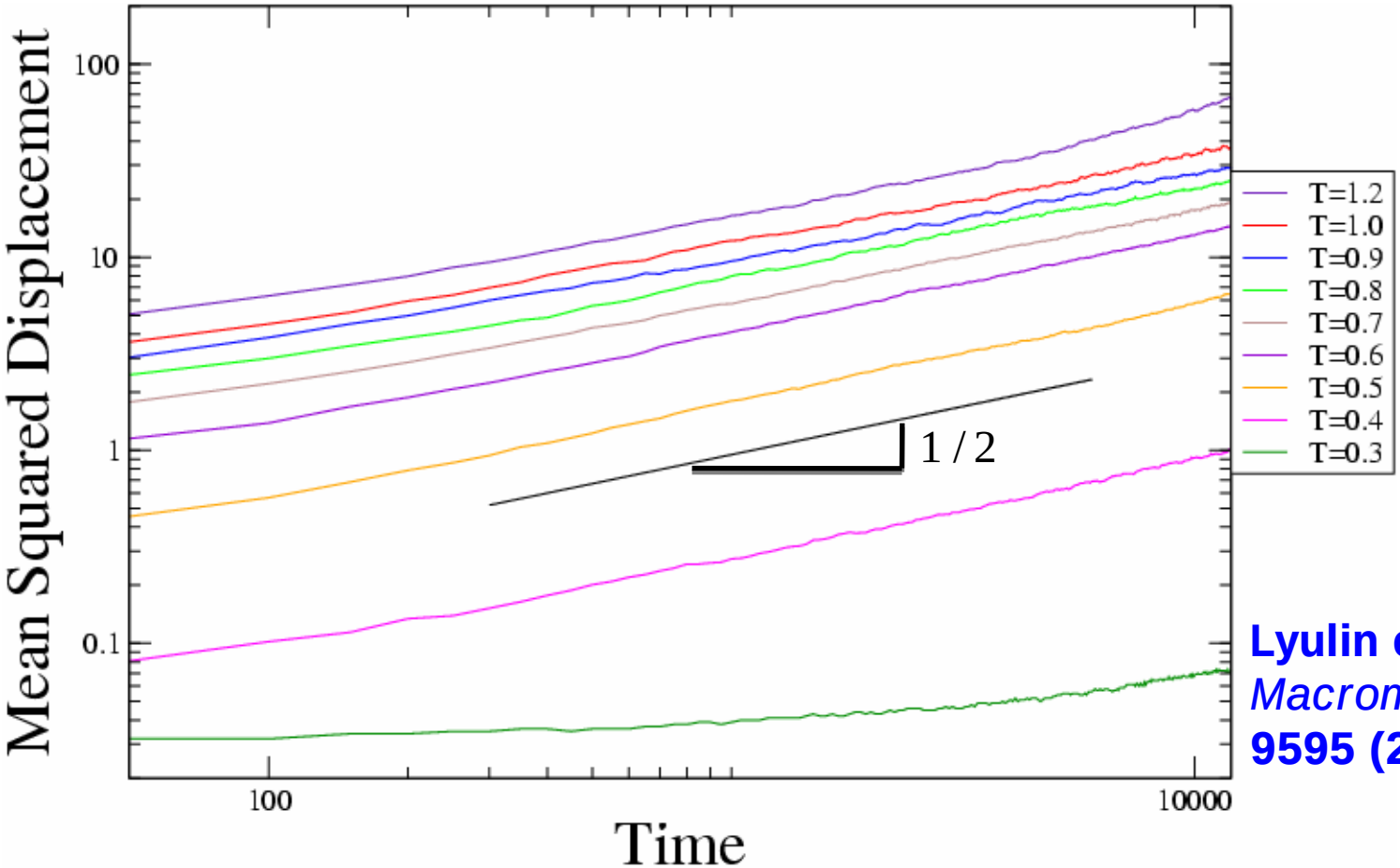
Glass Transition: ellipsometry



$T_g = 0.5$

Temperature dependence of film thickness

Glass Transition: mobility



MCT:
T_{MCT}=0.36

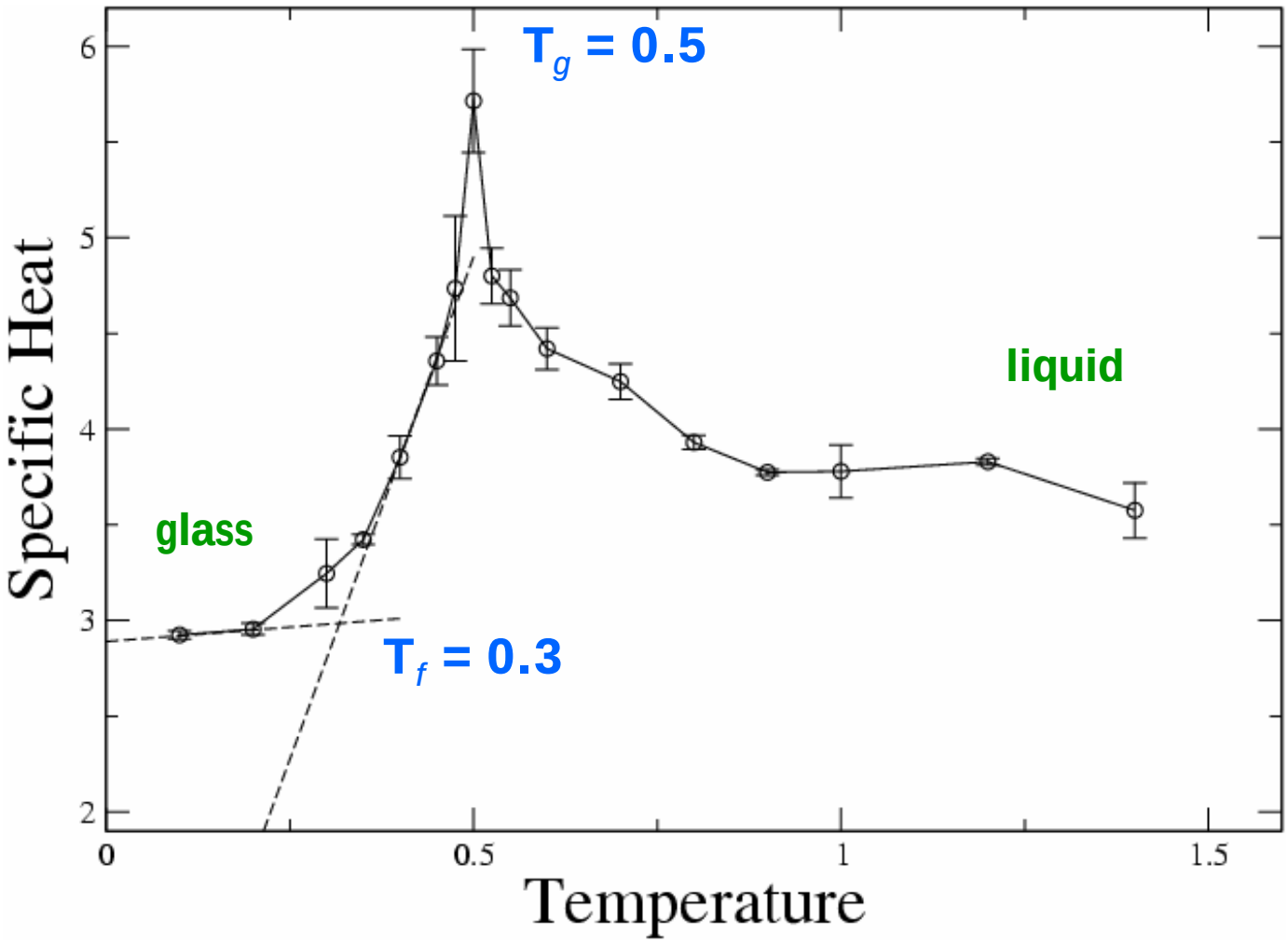
Lyulin et al., *Macromolecules* **9595 (2002)**

$$\left\langle \Delta r^2(t) \right\rangle \approx (D(T)t)^{0.5}$$

Relaxation time

$$\tau(T) = 1/D(t)$$

Glass transition: calorimetry



$$c_p = \frac{\left\langle (\Delta E)^2 \right\rangle}{NT^2}$$

T_f : fictive temperature

Temperature dependence of heat capacity

Summary 1

- **Glass transition behavior of supported ultrathin polymeric films studied using coarse-grained LJ models.**

- **Two important transitions:**

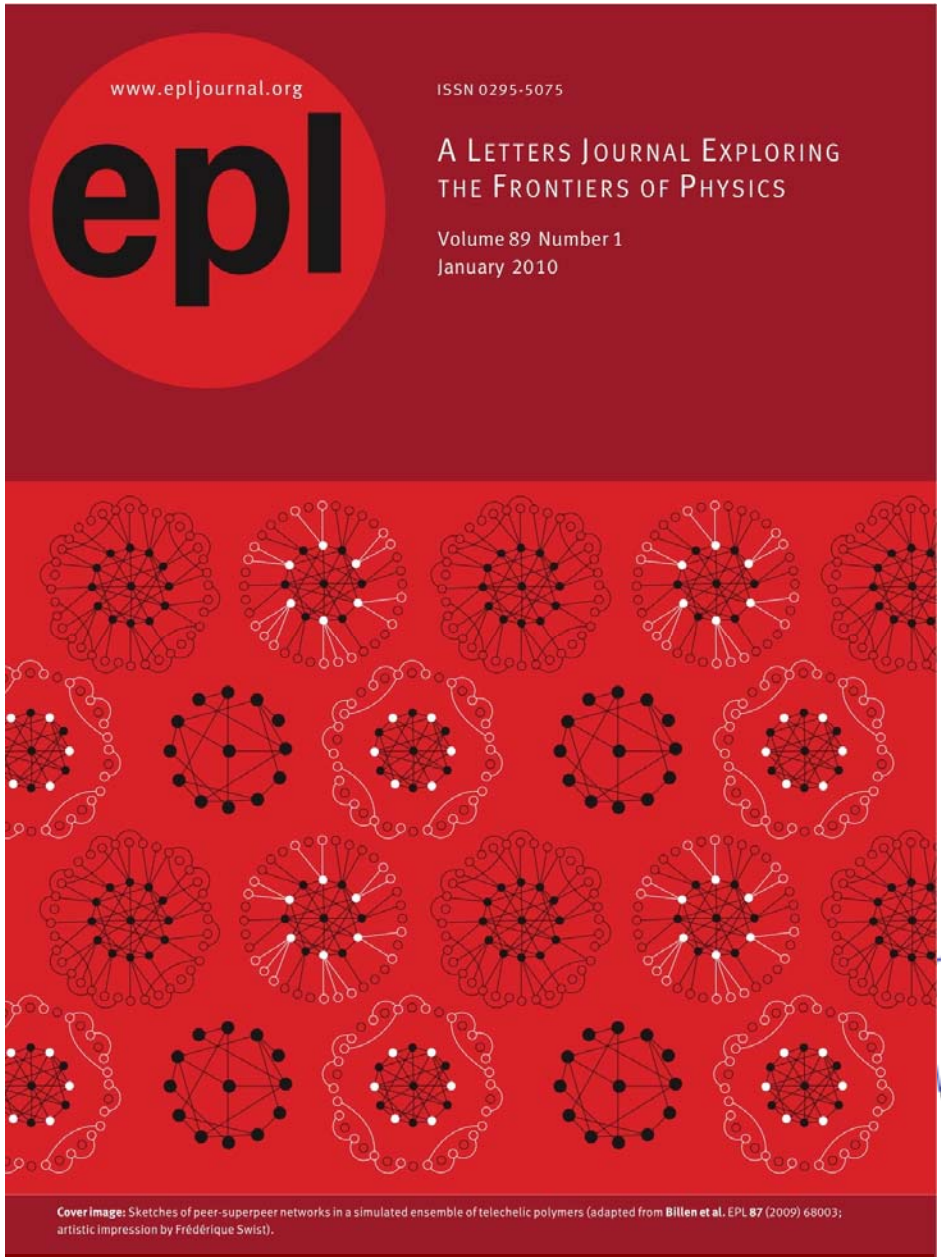
  1) **Structural Change:** $T_g = 0.5\ \varepsilon/k_B$

  2) **Dynamic Arrest:** $T_f = 0.3\ \varepsilon/k_B$

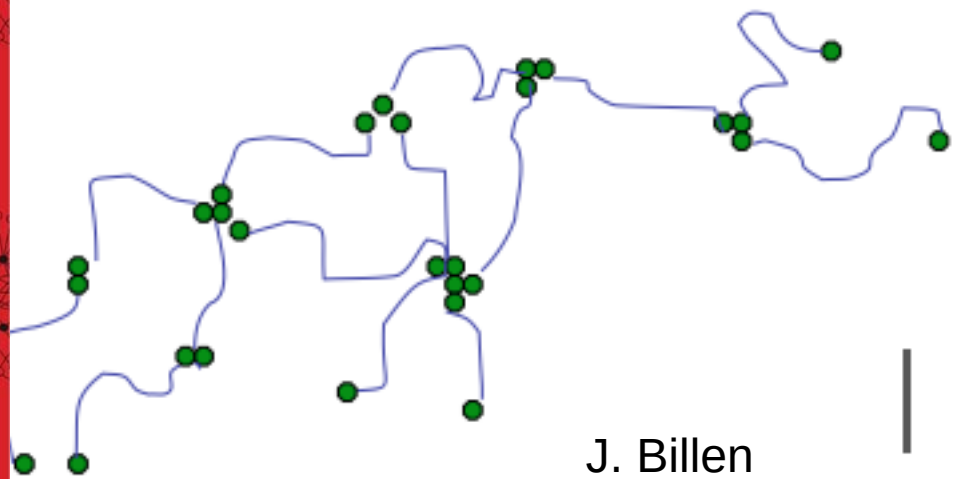
$T_{MCT} = 0.36\ \varepsilon/k_B$

$T_0 = 0.24\ \varepsilon/k_B$

Topology of Reversible Polymeric Network Gel

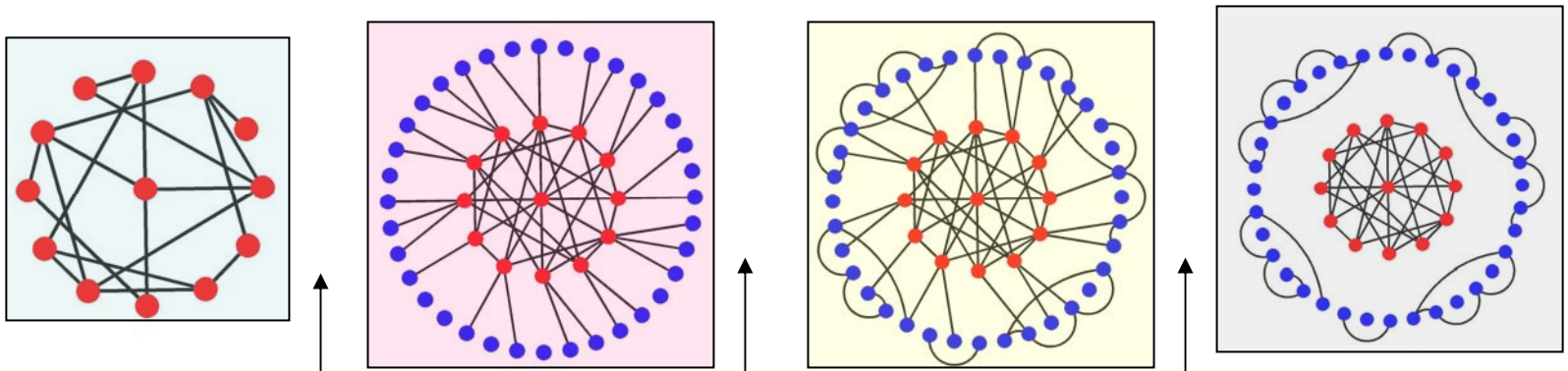


Billen et al. 87, 68203 (2009).

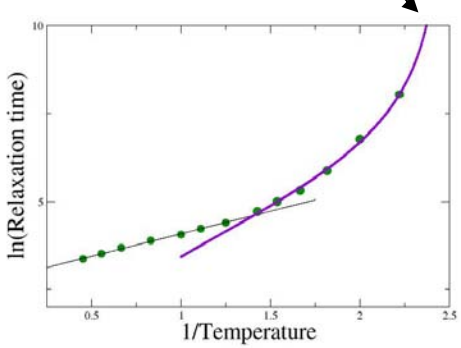


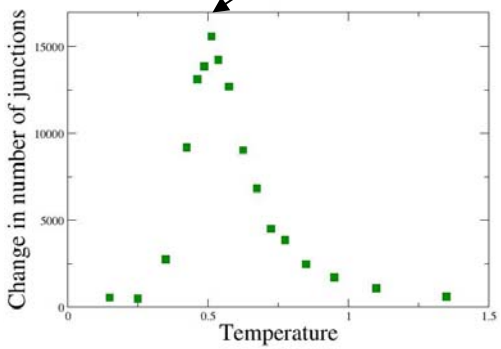
J. Billen
M. Wilson
A.Rabinovitch
A. Baljon

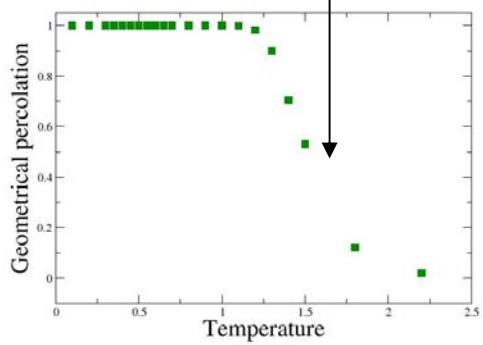
Transition temperatures



$T_c \approx 0.4$ $T_m \approx 0.5$ $T_p \approx 1.5$







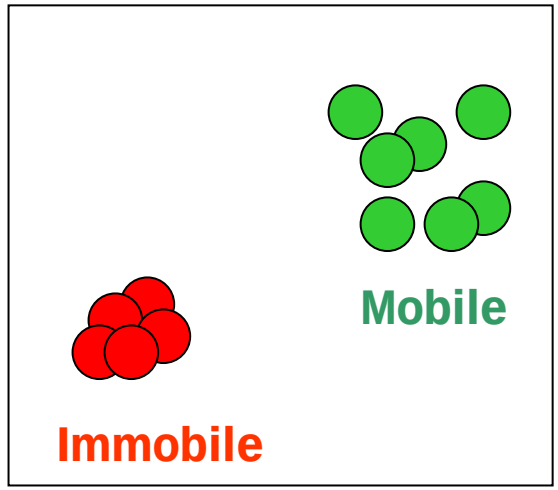
Dynamic arrest
Relaxation time τ diverges

Structural change
Micelle transition
Increase in number of associations

$$\frac{\partial^2 \Phi}{\partial T^2} = 0$$

Geometrical percolation

Dynamic Heterogeneities in Glassy Systems



Experiments

- Spiess and coworkers (1998)
- Ediger and coworkers (2000)
- Ellison and Torkelson (2003)

Theory

- Layer model
- Dynamic facilitation

(Garrahan and Chandler, 2003)

- Percolation of clusters with high local density

(Long and Lequex)

Simulations

- Mobile and immobile particles
- Mobile particles form strings and clusters

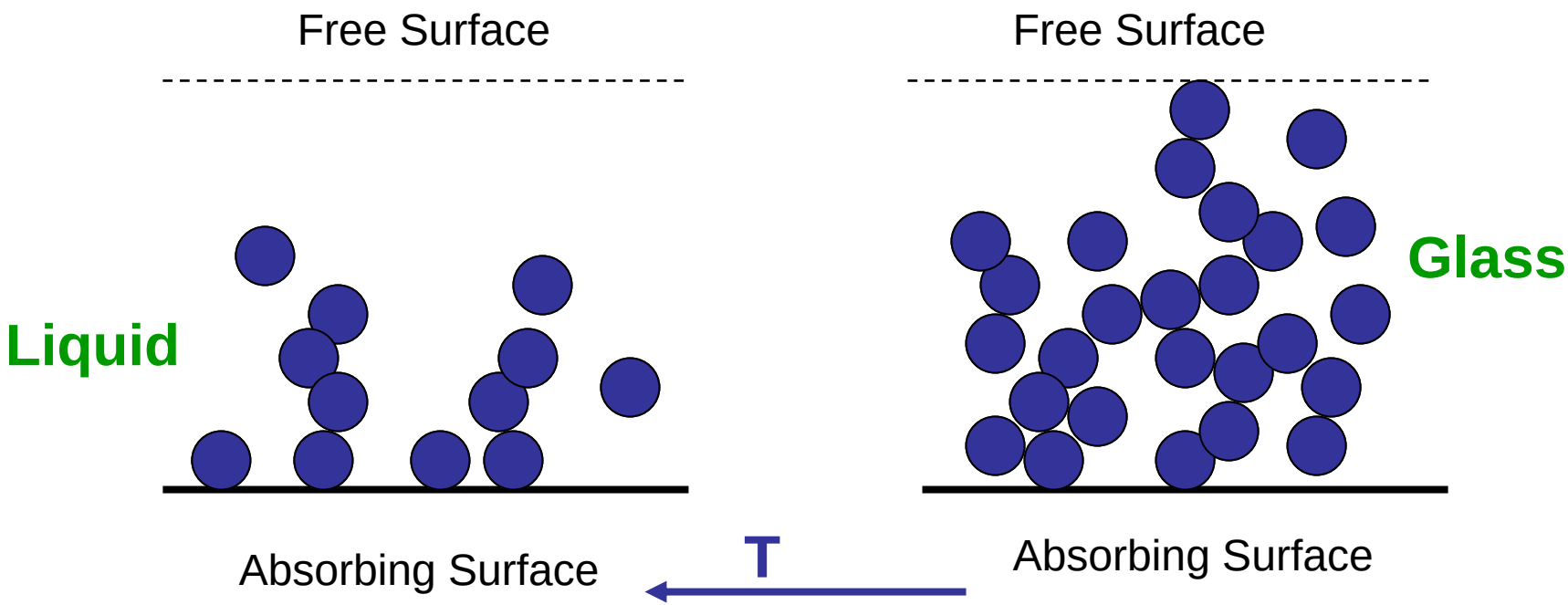
(Glotzer, Douglas and coworkers,)

Percolation model

- **CRR**- cooperatively rearranging region.
- Relaxation time of CRR (τ_K) depends on local density. ???? -local energy landscape, mobility.
- Above a threshold density ρ^*, τ_K is slower than the experimental timescale. (CRR is arrested)
- As the system cools the average density increases, and the probability that a CRR has a density above ρ^* increases.
- At the glass transition temperature the arrested CRRs percolate the system.
- Also can explain thin film behavior: Percolation threshold increases with system size in 3D (free standing films), decreases with system sizes in 2D (supported films with attractive interaction).

D. Long and F. Lequeux, *Eur. Phys. J. E* **4, 371 (2001)**

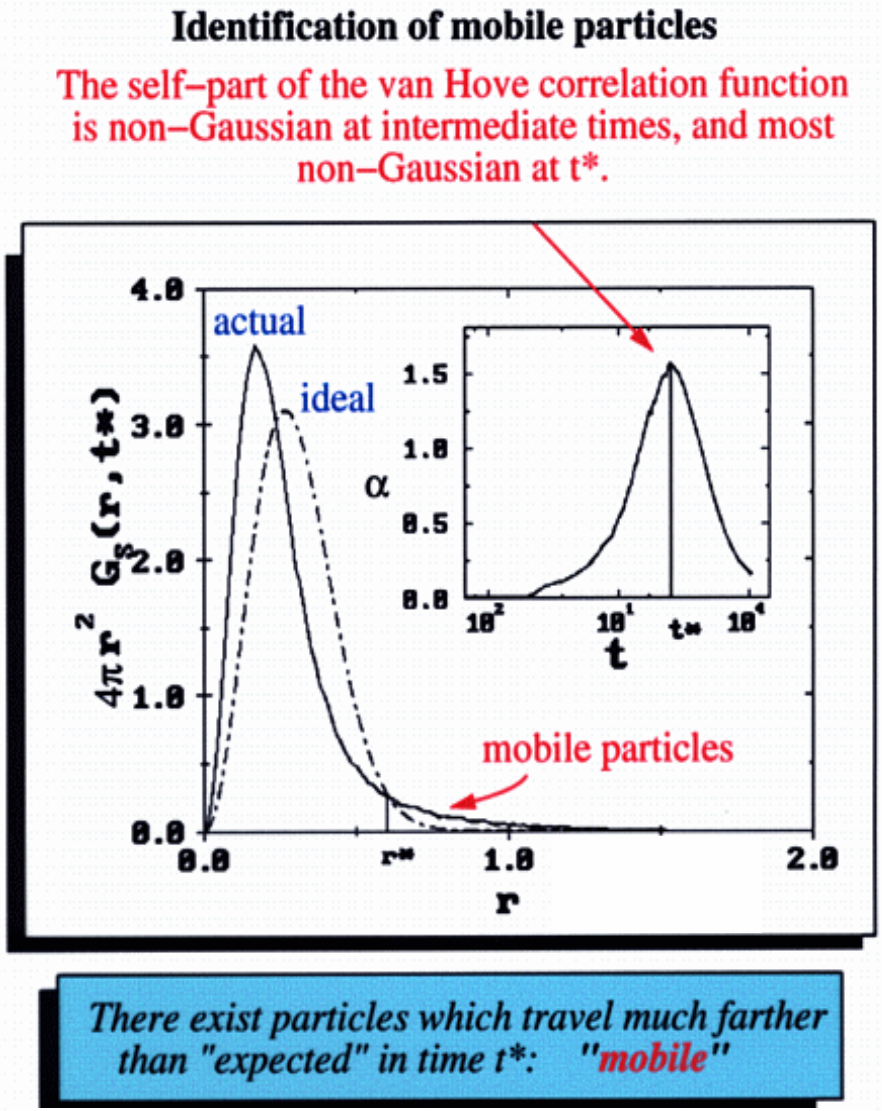
We: Percolation of Clusters of Slow Dynamics



Slow dynamics in regions of high local density?

T_g increases with decreasing film thickness

Spatially heterogeneous dynamics



van Hove correlation function

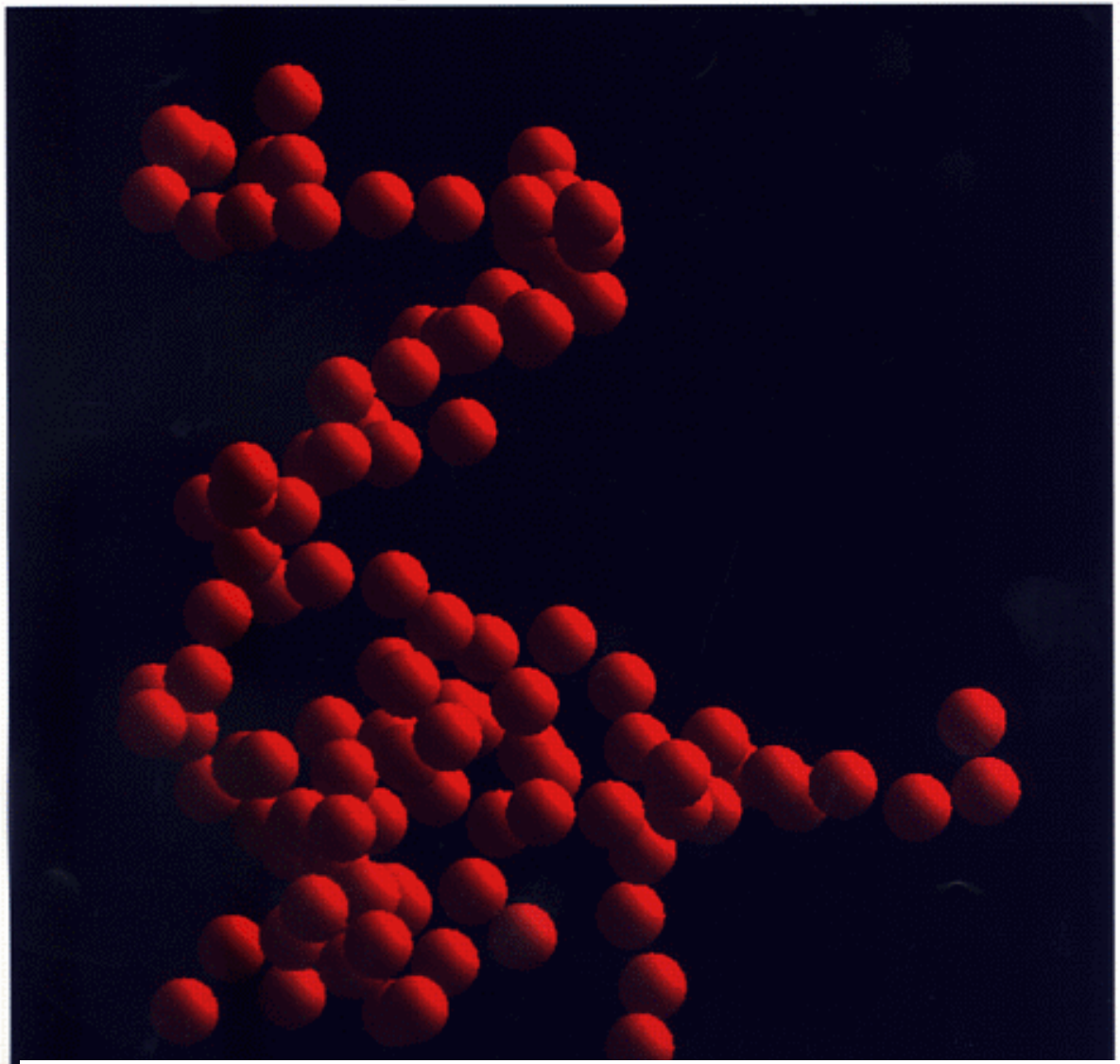
$$G_s(r,t) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \delta(\vec{r}_i(t) - \vec{r}_i(0) - \vec{r}) \right\rangle$$

$$\alpha = \frac{3\langle r^4 \rangle}{5\langle r^2 \rangle^2} - 1$$

S. Glotzer et al.

Snapshot of a large cluster of nearest–neighbor mobile particles in coldest run.

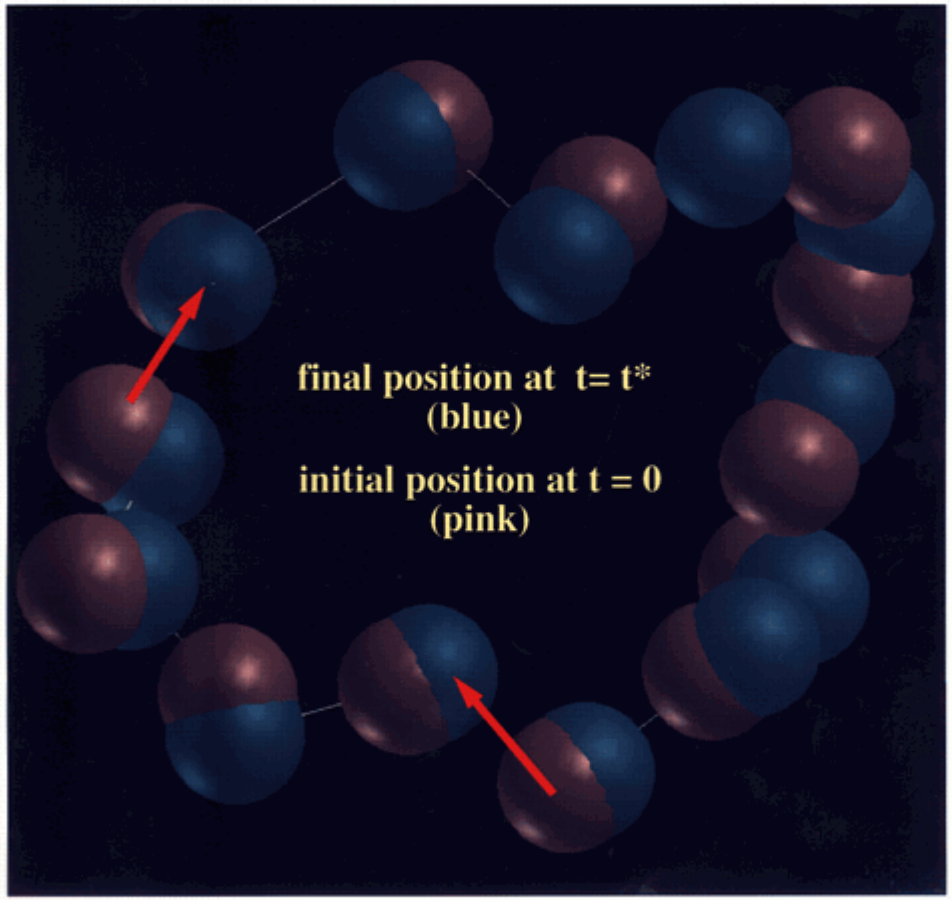
(The 7890 other particles in the liquid are not shown.)



S. Glotzer, Douglas et al.

A large loop of 13 molecules in the coldest run at two different times.

(The 7987 other particles in the liquid are not shown.)



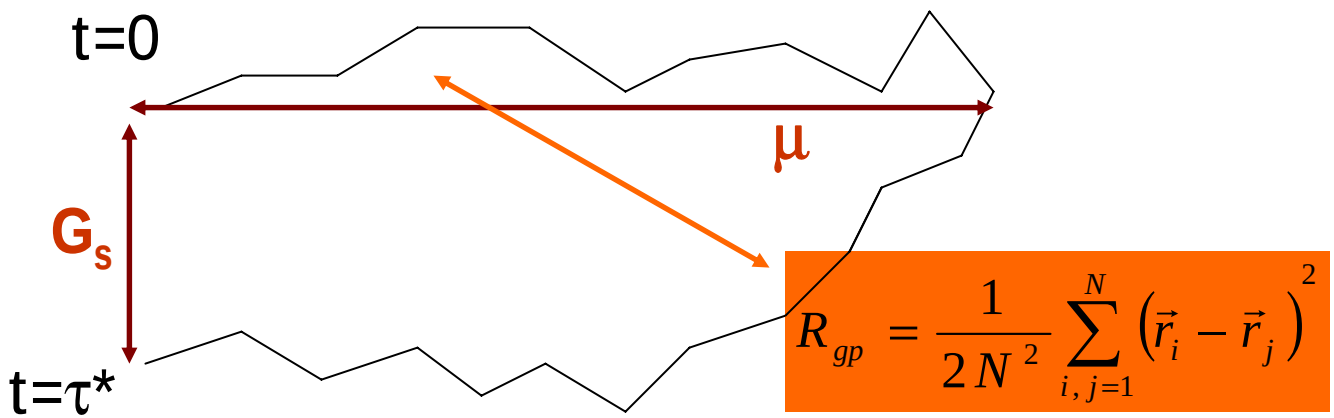
Particles move cooperatively in strings.

S. Glotzer, Douglas et al.

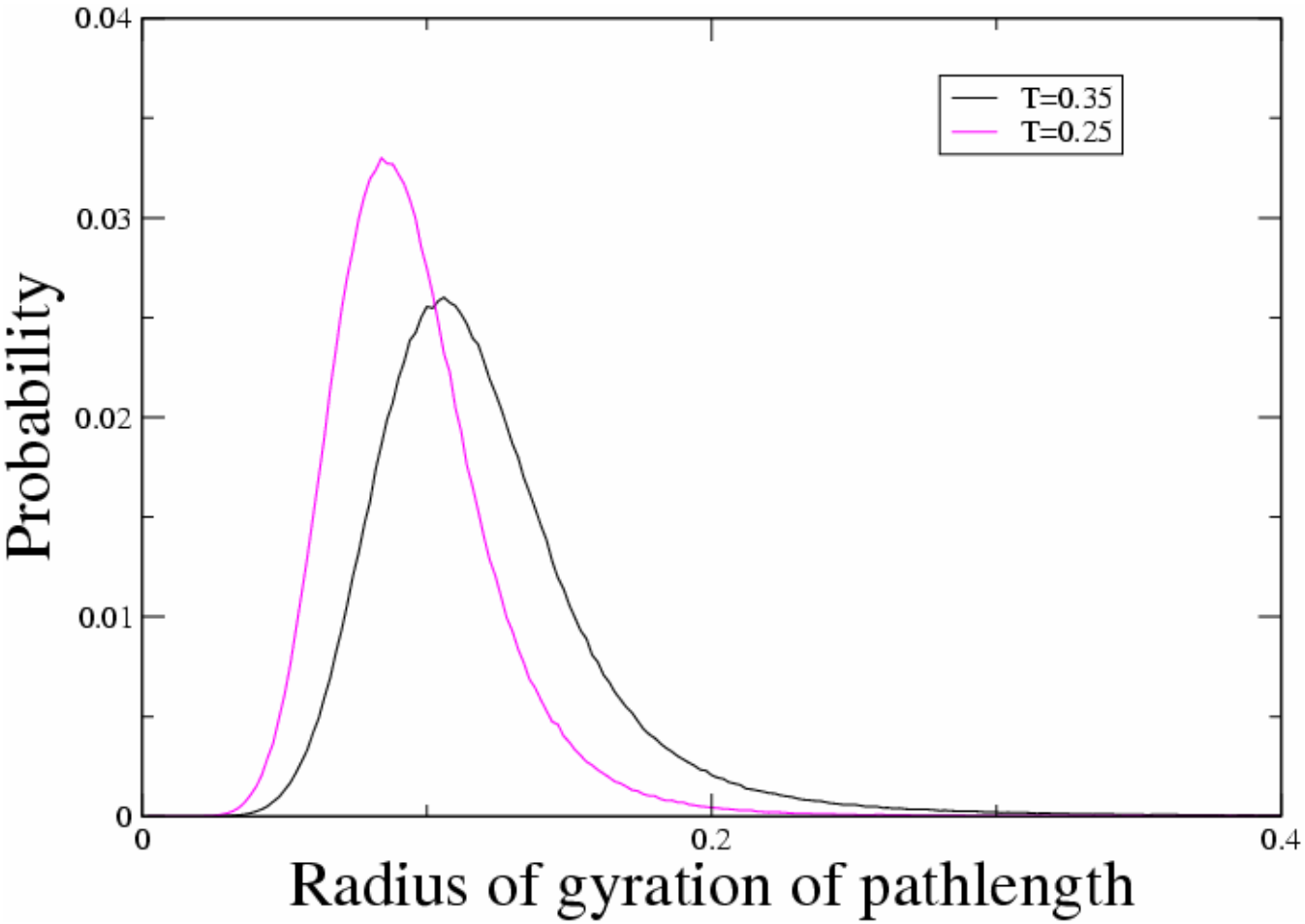
Characterization of Bead Mobility

Definitions of Mobility

- van Hove (total displacement) G_s
- Maximum displacement μ
- Radius of gyration of the path length R_{gp}



Heterogeneous dynamics in thin films



$t^*=5\ \tau$

Definition of Immobile Clusters

Lindemann Criterion for Melting

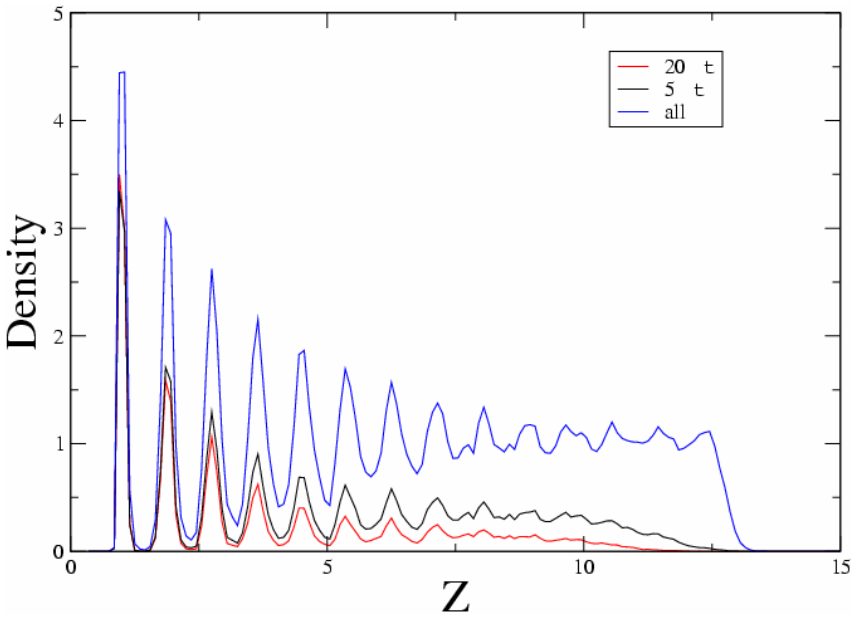
Crystalline solids melt when the rms displacement of atoms is 0.1~0.15 in terms of lattice units

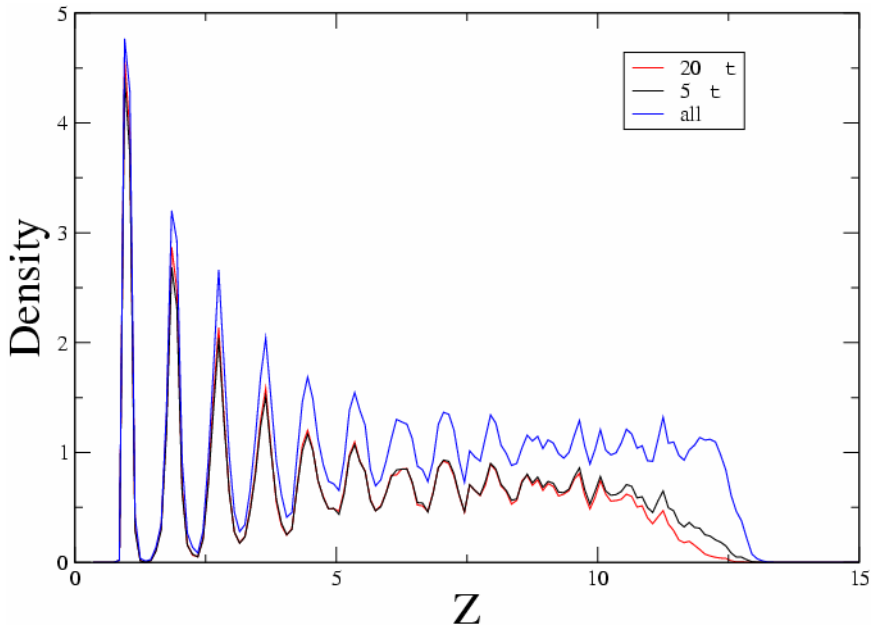
Immobile: $R_{gp} < 0.1\ \sigma$

- **Cluster**

Connect immobile beads when their separation is less than 1.45 σ (first minimum in radial distribution function)

Distribution of Immobile Beads





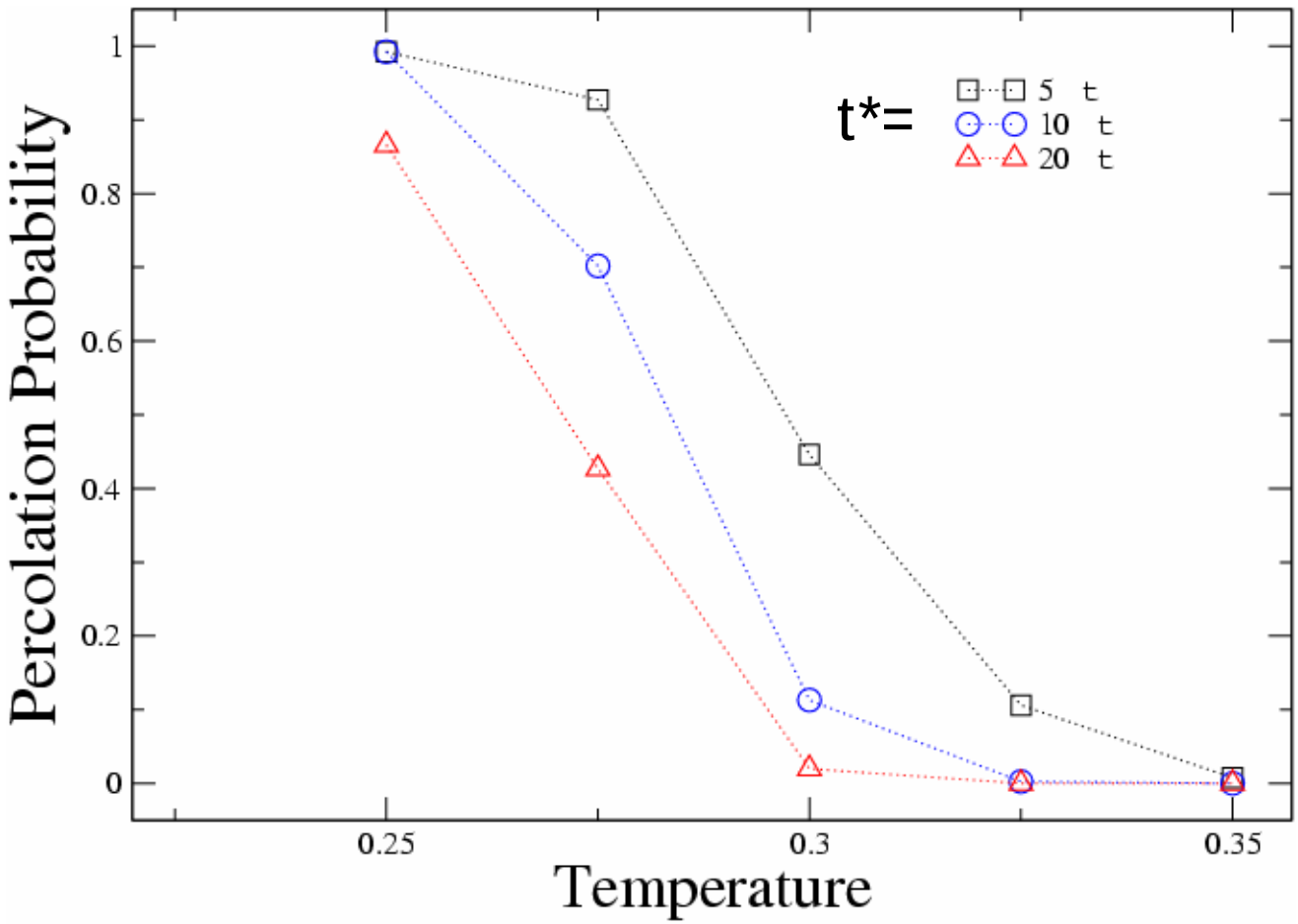
T = 0.35

T = 0.25

t^*=5, 20 τ

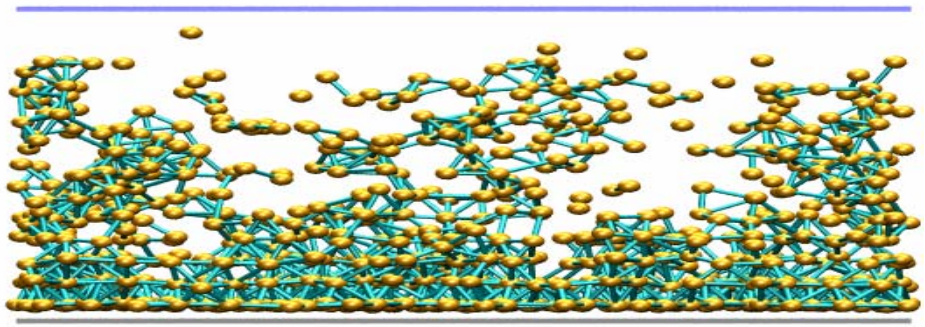
Immobile beads are distributed over the **entire** film

Percolation Transition

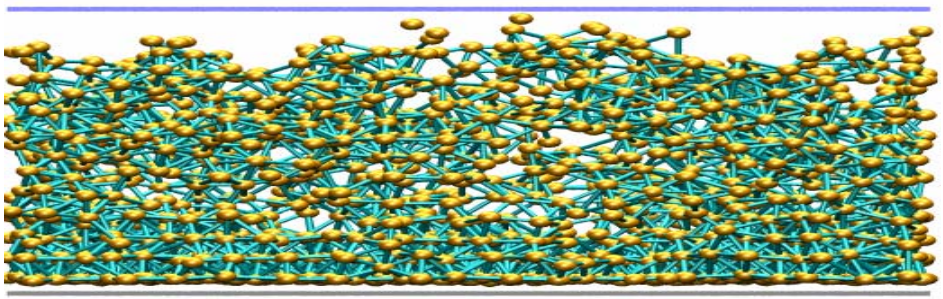


Transition occurs over a small temperature range

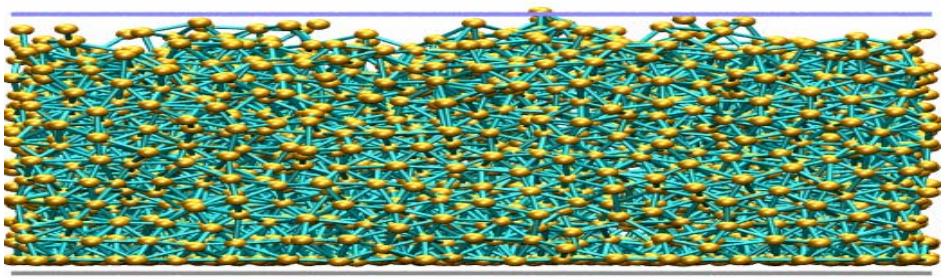
T= 0.35



T= 0.3



T= 0.25

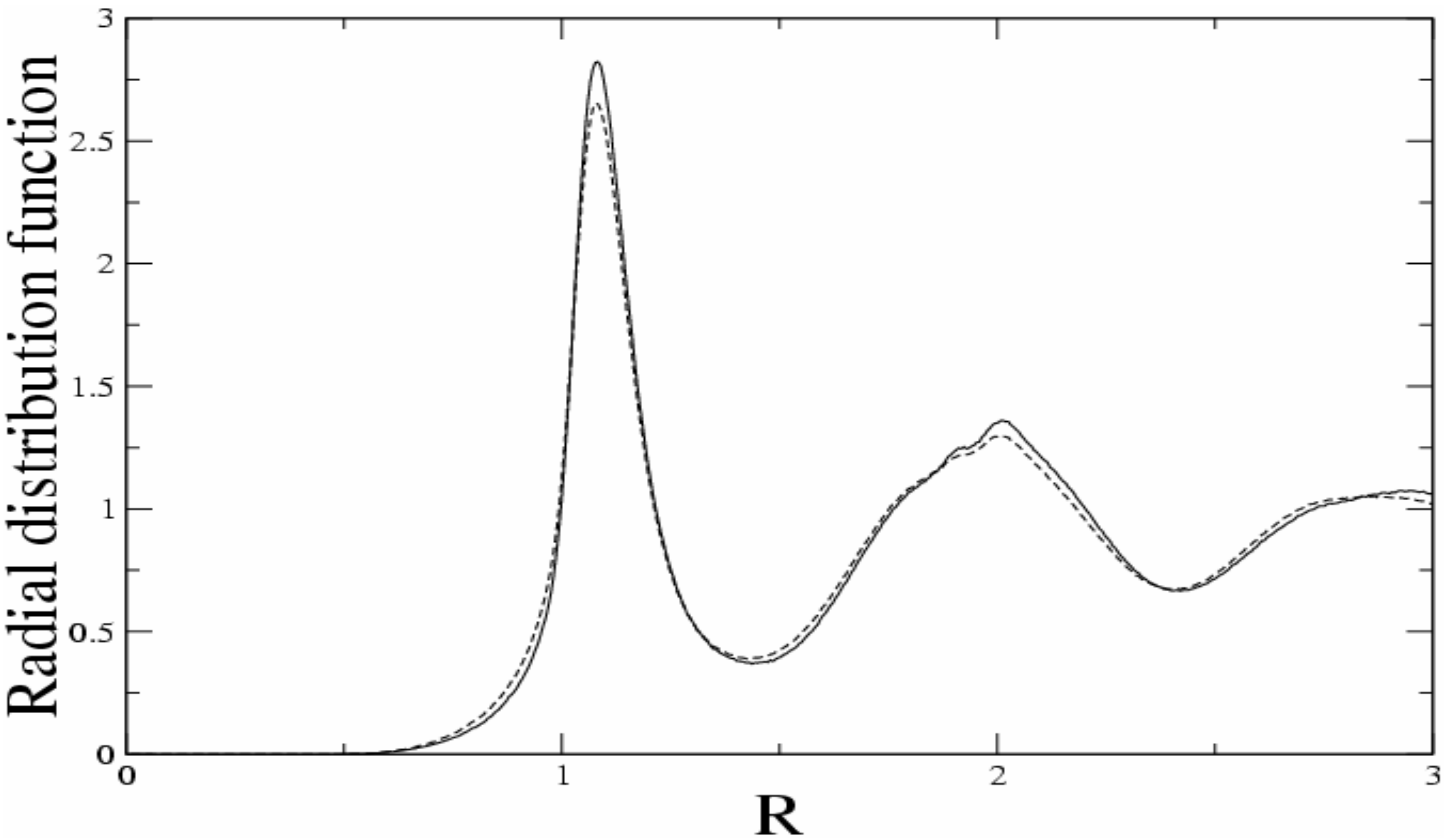


Immobile Clusters

Immobile particle

Connection between adjacent immobile particles in a cluster

Local Packing Near Immobile Beads



- Immobile beads .... All beads

Small differences in packing near mobile and immobile beads

Summary 2

- Supercooled films show dynamic heterogeneities
- Radius of gyration of particle path length used as a criterion of defining particle mobility
- Immobile beads occur throughout the film but their distribution is non-uniform
- Clusters of immobile beads percolate at temperatures close to the glass transition temperature

Recent work: local glass transition temperatures

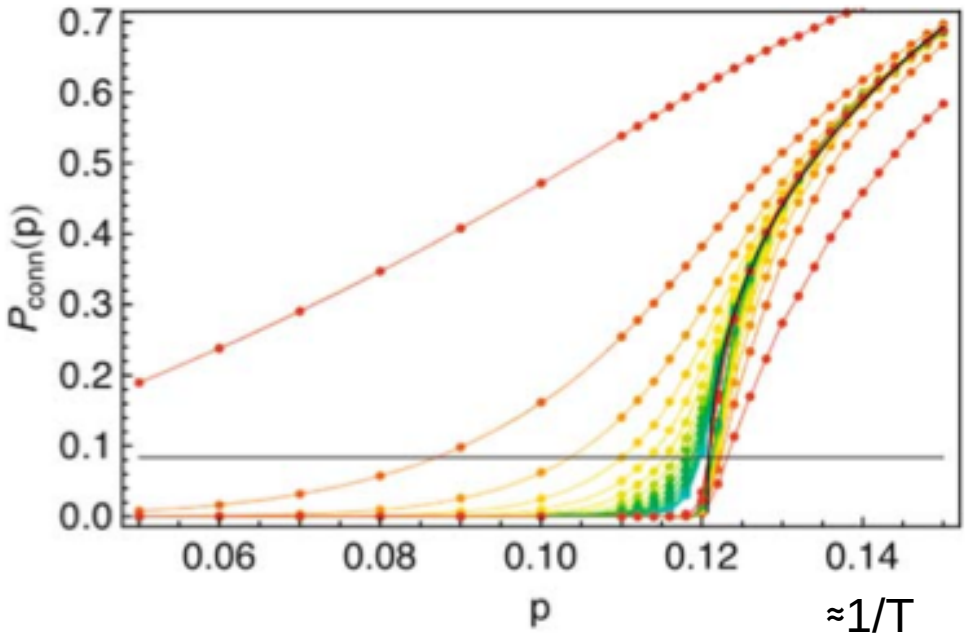


Fig. 1. (Color online) Probability P_{conn} of a site (CRR) in a given layer of an FCC lattice being part of a transversely spanning cluster, as a function of bond filling fraction p, for layers near a strongly interacting substrate (curves to left) or near a free surface (curves to right). Dark solid curve is result for sites far from any interface. Results shown are for near-substrate layers $z = 2, 4, \ldots$, and near-surface layers $z = n - 1, n - 3, \ldots$ Horizontal line is $P_{conn} = 1/Q$.

Experiments: Torkelson et al.
local T_g values:

- middle of film: T_g^{bulk}
- close to interface:
  T_g(z=distance to interface)

p = number of arrested CRRs.
$P_{conn}(z)$ = probability that an arrested CRR is part of a transversely spanning cluster.

Good agreement with experiments near absorbing substrate.
No agreement with experiments near free surface.

Lipson and Milner, *Eur. Phys. J. B* **72, 133 (2009)**

Recent work: percolation of regions of mobility in configuration space

- Hard spheres
- Allowed regions in configuration space
- When they percolate: glass transition
  - complete structural relaxation
  - intermediate scattering function for t ➔ ∞ becomes zero.

-For infinite system size $\phi_{P=}\phi_{J.}$

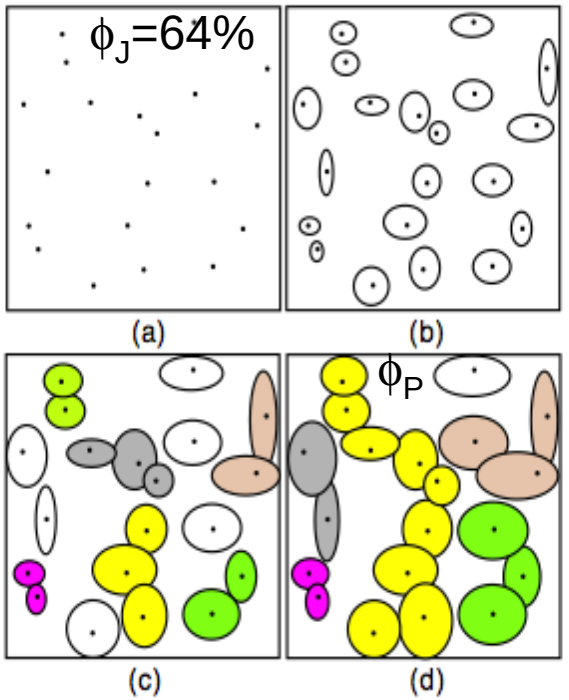


FIG. 1 (color online). Schematic of allowed regions in configuration space for hard spheres. (a) At ϕ_J only CJ states (points) are allowed; (b) At $\phi_1 < \phi_J$ motion occurs in closed mobility domains surrounding CJ states; (c) At $\phi_2 < \phi_1$ transitions between contacting mobility domains (shaded) occur; (d) At $\phi_P < \phi_2$ at least one network of mobility domains percolates (shaded yellow) and the system transitions from glass to metastable liquid.

O'Hern et al., *PRL* 102, 015702 (2009)