Approaching the Glass Transition: The Importance of Near-Mean Field

WPI
Physics Colloquium

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Outline

- Review laboratory and computer experiments on glasses and current theoretical understanding.

  No consensus on important properties of a glass and no generally accepted model of a glass.

- Introduce simple near-mean-field model.

- Molecular dynamics simulations of Lennard-Jones system.

- Glass transition in *mean-field* and *near-mean--field* systems can be associated with a liquid-to-solid *spinodal* and *pseudospinodal*, respectively.

  Conclusion: There is a class of materials for which the glass transition can be identified with an underlying *thermodynamic instability*.

Importance of Glasses

a fascinating and mysterious form of matter
liquid that has lost its ability to flow

Cool liquid to below freezing temperature.
$\Rightarrow$ supercooled liquid
or crystalline solid
or glass

Technological significance
Unlike the transition between liquid water and ice, the glass transition is not abrupt — no sharp change in volume or other properties. Can exploit this property by, for example, replacing water in living embryos by a glass forming liquid and preventing damage from expansion during freezing. Many materials are glasses formed of metal alloys.

Theoretical significance
A glass serves as a starting point for understanding complex systems – systems with many components which interact with varying strengths, leading to complex behavior.

Summary of Conventional Wisdom

- Viscosity η becomes very large.

  empirical definition of T_g: $\eta \approx 10^{15}$ poise

  $$\eta \sim \eta_0\, e^{A/(T-T_0)} \qquad \text{(Vogel-Fulcher)}$$

- Abrupt decrease in C_P.

  Fragile glass formers: large jump in $C_P \to T_0 \neq 0$

  Strong glass formers: small jump in $C_P \to T_0 \approx 0$

  "Notwithstanding the arguments for an underlying phase transition, it is generally agreed that . . . glass transition . . . is strictly kinetic in origin."

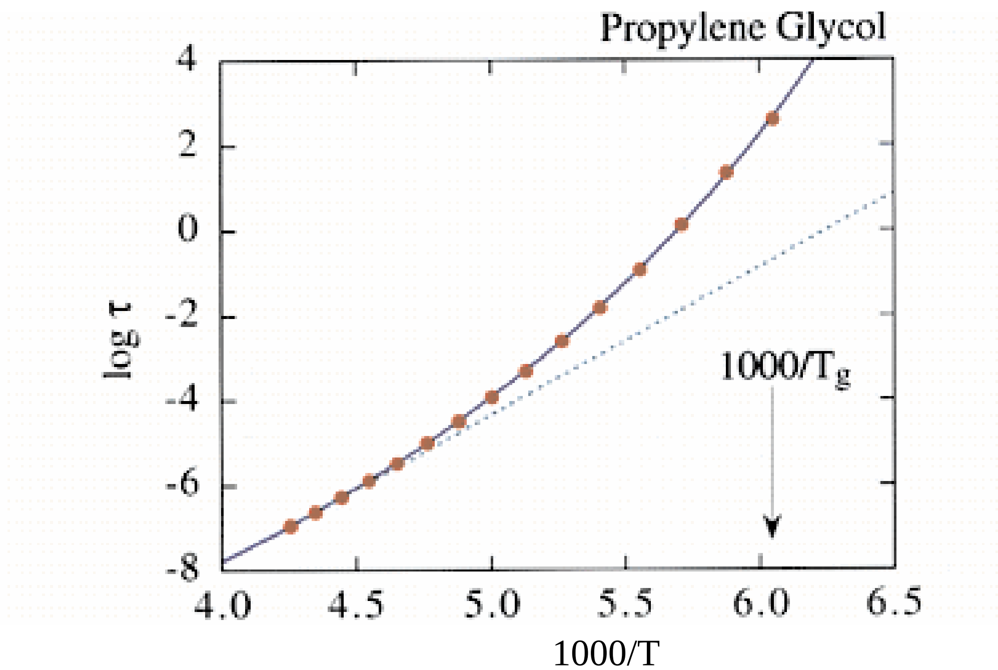
  I will discuss only *fragile glass formers*.

- Self-diffusion coefficient $D \to 0$.

- Slow relaxation processes.

$$C(t) = e^{-(t/\tau)^{\beta}} \qquad \beta \approx 0.5$$

$$\tau \sim e^{A/(T-T_0)}$$



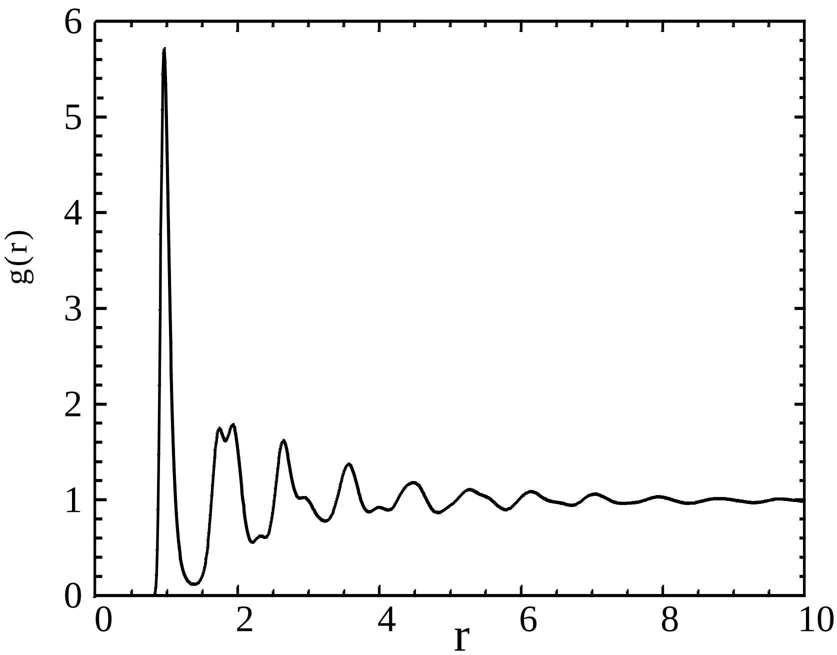
$T_0 = 120\,\mathrm{K}$, $T_g = 160\,\mathrm{K}$

- History dependence – T_g depends on quench rate.

- Kauzmann paradox.

  extrapolation of entropy of supercooled liquid $\Rightarrow S_{\text{liquid}} < S_{\text{solid}}$ for $T < T_K$.

- Glass is disordered – split second peak of $g(r)$.



- Universal behavior of dielectric susceptibility $\epsilon''(\omega)$ (Nagel and co-workers).

  $\epsilon''(\omega)$ can be fitted to a universal function over 13 orders of magnitude of ω.

$$\epsilon''(\omega) = C_1\omega^{-\beta} + C_2\omega^{-\sigma}$$

  β and σ decrease as $T \to 0$.

- Scaling form of $\epsilon''(\omega)$ implies divergent static susceptibility at $T = T_0$. Similar behavior found for dipolar spin glass.

- Experimental evidence for spatially heterogeneous dynamics in supercooled liquids.

Spier	NMR
Ediger	Selective photobleaching
Israeloff	Scanning probe microscopy
	Typical size of "slow" region is 5 nm.

- Simulation evidence for spatially heterogeneous dynamics in supercooled liquids.

  "String-like Clusters and Cooperative Motion in a Model Glass-Forming Liquid," Donati, Douglas, Kob, Plimpton, Poole, and Glotzer, *Phys. Rev. Lett.* **80**, 2338 (1998).

Some Outstanding Questions

1. Is the glass transition a thermodynamic phase transition or a dynamical effect?

   Characteristic relaxation times increase as T is lowered and eventually exceed observation time. Hence, it is difficult to distinguish a thermodynamic glass transition from a kinetic transition.

2. What is the structure of a glass? Does a glass differ from a "frozen" liquid?

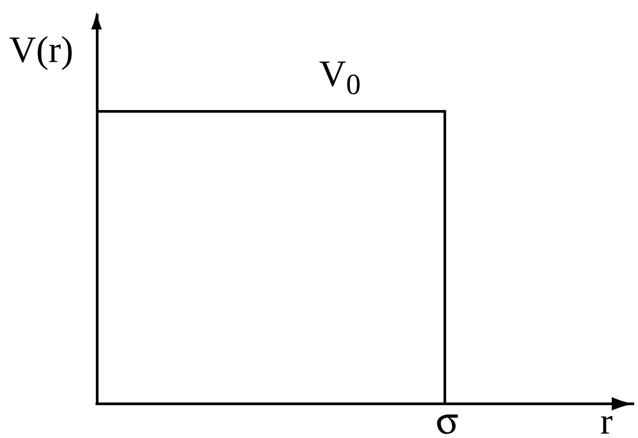
3. What is origin of the observed scaling behavior in $\epsilon''(\omega)$?

4. What is the connection, if any, between the slow dynamics in glasses and the slow dynamics in granular matter and other "jammed" states?

Mean-field Model of a Structural Glass Transition

No well accepted theoretical perspective.

Repulsive step potential



- mean-field: $V_0 \to 0$, $\sigma \to \infty$, $V_0 \sigma^d = \text{const}$

  near-mean-field: $\rho \sigma^d >> 1$

- At high T uniform density fluid state (Grewe and Klein)

- Instability (spinodal) at $T = T_s$ at fixed ρ.

- Uniform density state becomes unstable to fluctuations at nonzero wave vector k_0. Stable phase becomes fcc solid of "clumps."

What happens when we quench from $T > T_s$ to $T < T_s$?

(Klein, Gould, Ramos, Clejan, and Melcuk, Physica 1994)

Results of MC simulations at $\sigma = 3$ and $\rho = 1.95$. System is *near-mean-field*.

- Number and mass of clumps depends on quench history.
- Number of clumps does not change with time.
- Centers of mass of clumps do not diffuse.

  $\Rightarrow$ system no longer ergodic at clump level.
- Theory: $D > 0$ for $T > 0$. Simulations: $D \to 0$ as $T \to T_{\text{kin}}$. T_{kin} depends on length of run.

  $\Rightarrow$ system ergodic on particle level until kinetic transition at $T = T_{\text{kin}}$.

- Multiple free energy minima (many disordered and few crystalline clump configurations).

  suggests existence of *metastable glass phase*

  glass/spinodal transition $\rightarrow T_s$

Spinodal is similar to critical point. Hence, expect critical slowing down, divergent correlation length, clusters of all length scales, and divergences of various quantities.

Can we see analogous behavior in more realistic systems?

Spinodals and Pseudospinodals

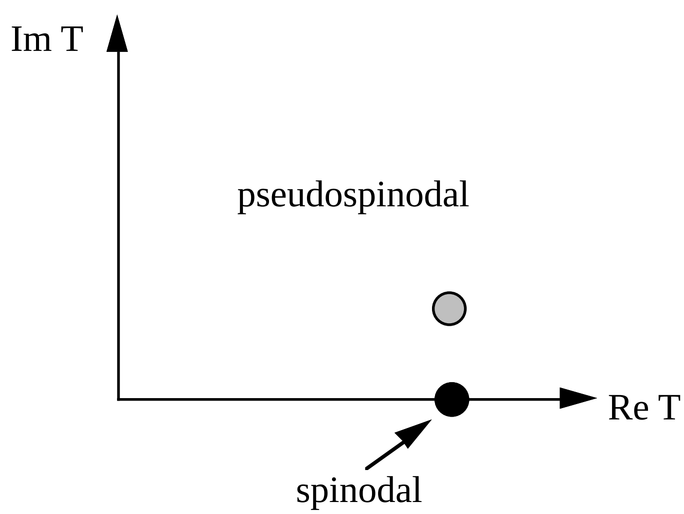
Spinodal is a line of critical points.

Observe mean-field critical behavior in the limit of infinite-range potential.

divergent quantity	γ	location
$\chi(k=0) \sim (T-T_c)^{-\gamma}$	1	Ising critical point
$\chi(k=0) \sim (T-T_s)^{-\gamma}$	1	Ising spinodal
$\chi(k_0>0) \sim (T-T_s)^{-\gamma}$	1	Liquid-solid spinodal

What happens when range of potential is long, but not infinite? Observe *pseudospinodal*.

Singularity affects system if it is close enough to the real axis and can lead to apparent critical phenomena and near mean-field effects.



Analogies to critical point and pseudospinodal in Ising models

- Existence of critical point and spinodal imply the existence of clusters, but rigorous definition of clusters exists only near the Ising critical point and Ising spinodal. What can we learn by analogy to the Ising model?

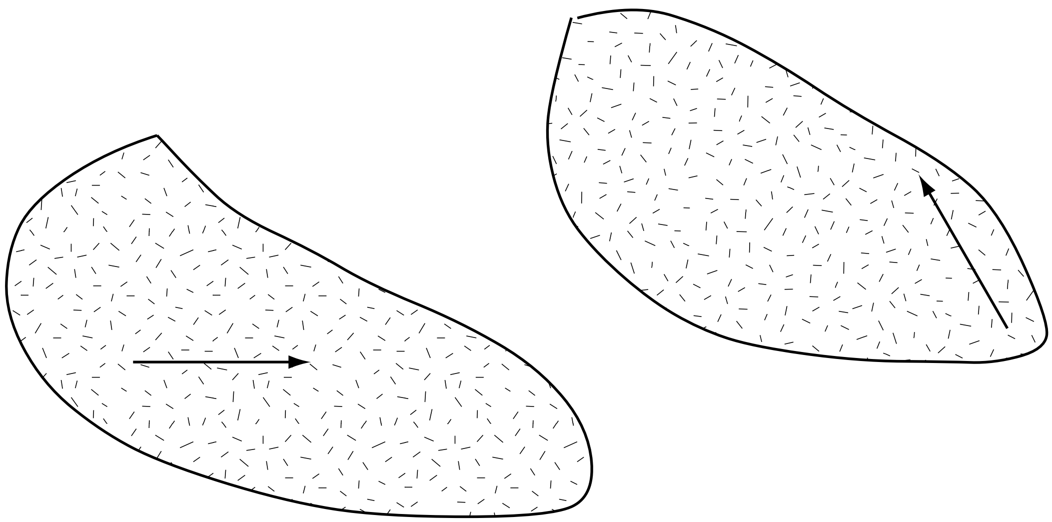
- Near Ising critical point, critical fluctuations and clusters are identical.

- Near the mean-field Ising critical point and spinodal, must distinguish between critical phenomena fluctuations and clusters. The fluctuations in the number of clusters are the critical phenomena fluctuations. That is the critical fluctuations are an incoherent superposition of overlapping but independent clusters.

- Near the spinodal lifetime of clusters is zero. Near the pseudospinodal lifetime is finite, but considerably shorter than the lifetime of the critical phenomena fluctuations.

Implications for Liquid-Solid Pseudospinodal

- Liquid-solid pseudospinodal at $k \neq 0$.
- Critical fluctuations are an incoherent superposition of overlapping clusters, each of which has a spatial symmetry.



Suppression of divergence occurs for $k \neq 0$ peak, but not for a mean-field critical point which occurs at $k = 0$.

- For near-mean-field systems clusters have finite lifetime; zero lifetime for mean-field systems.

Implications for Liquid-Solid Pseudospinodal II

- Mean-field prediction:

$$S(k_0) \sim (T - T_s)^{-1} \quad \text{all d}$$

- Near-mean-field predictions:

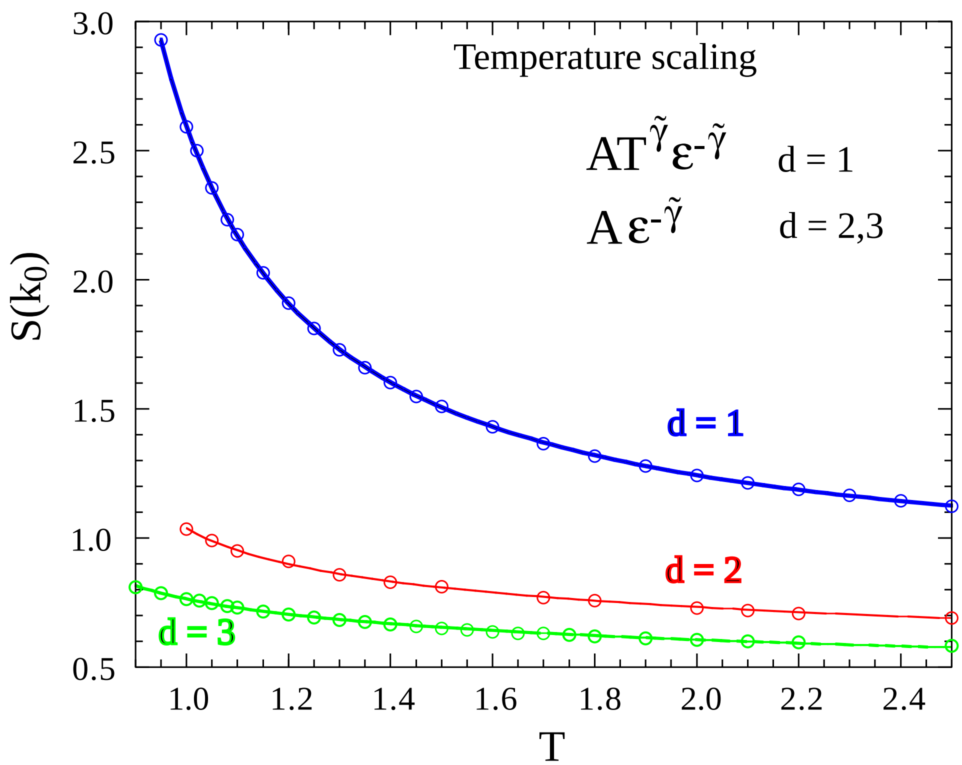
$$S(k_0) \sim (T - T_s)^{-\tilde{\gamma}}$$

$\tilde{\gamma}$	d
1	$d = 1$
$1/2$	$d = 2$
0	$d \geq 3$

- Should recover $\tilde{\gamma} = 1$ if can make a measurement over time longer than lifetime of clusters.

MC simulations for step potential

d	N	R	σ	MCS	$\tilde{\gamma}$
1	10^4	48	0.05	10^5	1.02
2	10^3	6	0.15	10^5	0.44
3	10^3	3	0.45	$2–4 \times 10^5$	0.16 or log



Klein, Gould, Tobochnik, Alexander, Anghel, and Johnson, "Clusters and fluctuations at mean-field critical points and spinodals," *Phys. Rev. Lett.* **85**, 1270–1273 (2000); cond-mat/0001230.

Molecular Dynamics Simulations of Lennard-Jones potential

Further test of pseudospinodal interpretation: Scaling of clusters near pseudospinodal.

Clusters in step potential model difficult to identify because they consist of clumps which contain $\sim$ 100 particles.

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

Need two components to inhibit nucleation.
Melcuk et al., *Phys. Rev. Lett.*, **75**, 2522 (1995). Johnson et al., *Phys. Rev.* E **57**, 5707 (1998).

2D system
80% A, 20% B, $\sigma_A = 1.0$, $\sigma_B = 1.5$, $\sigma_{AB} = 1.25$, $\rho = 0.95$
duration of run: 10^{-7}–10^{-6} s, $\Delta t = 0.005$.

3D system (Kob-Andersen model)
80% A, 20% B, $\rho = 1.2$

interaction	σ	ϵ
AA	1.0	1.0
AB	0.8	1.5
BB	0.88	0.5

Predictions of Pseudospinoodal Interpretation

- Existence of pseudocritical point (the pseudospinodal) implies existence of cluster scaling and diverging correlation length.

- T close but not too close to T_s:

  $n_s \sim s^{-3/2}$ # of clusters of s particles

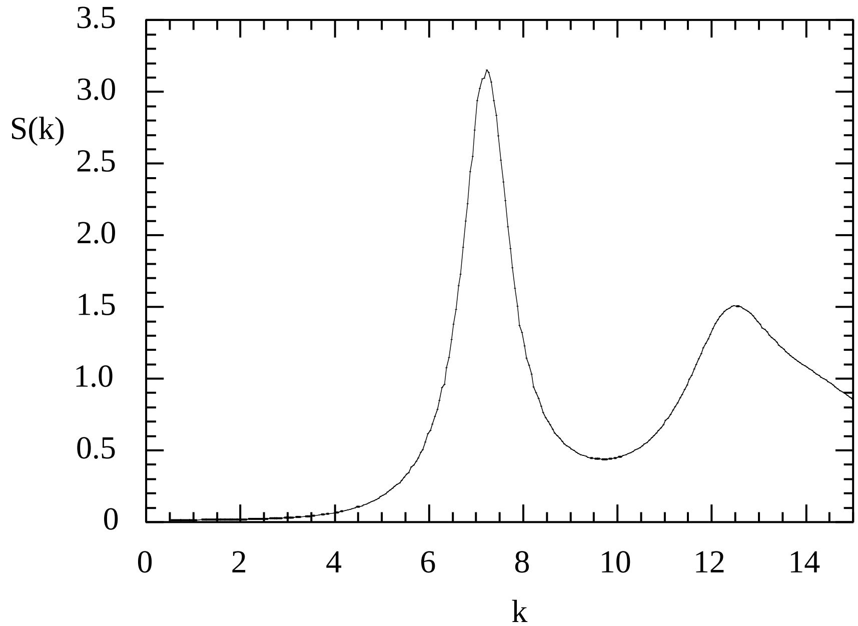
  Exponent 3/2 due to presence of *critical (mean-field) fluctuations*.

- T close to T_s:

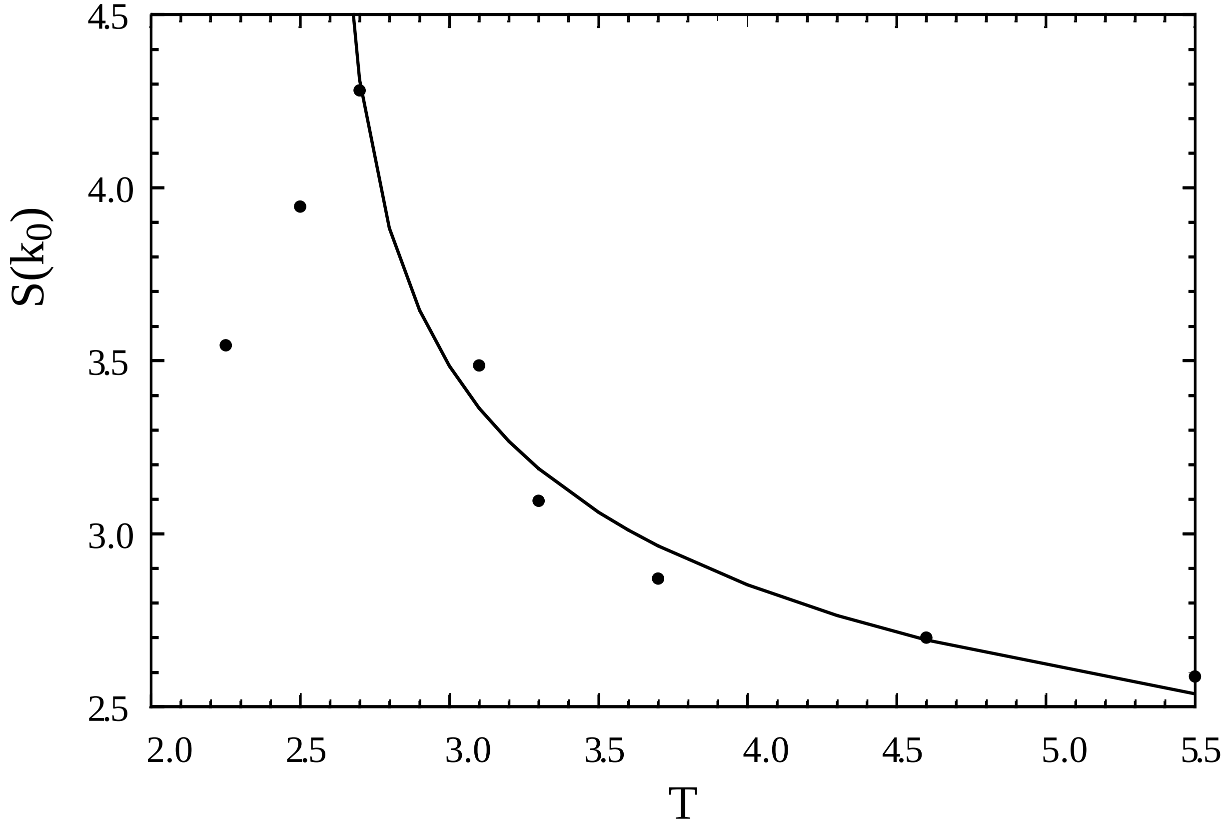
  $$n_s \sim s^{-2}$$

  Larger clusters formed by *arrested nucleation events*. System no longer in equilibrium, but self-diffusion coefficient $D > 0$.

Apparent Divergence of peak of $S(k)$ in 2D



Height of $S(k_0)$ increases as lower T.
width of peak decreases as lower T.



$$S(k_0) \sim (T - T_s)^{-0.2}$$

$$\xi \sim (T - T_s)^{0.3}$$

Weak divergence at $T = T_s \approx 2.6$ disappears if T too close to T_s (Ginzburg criterion).

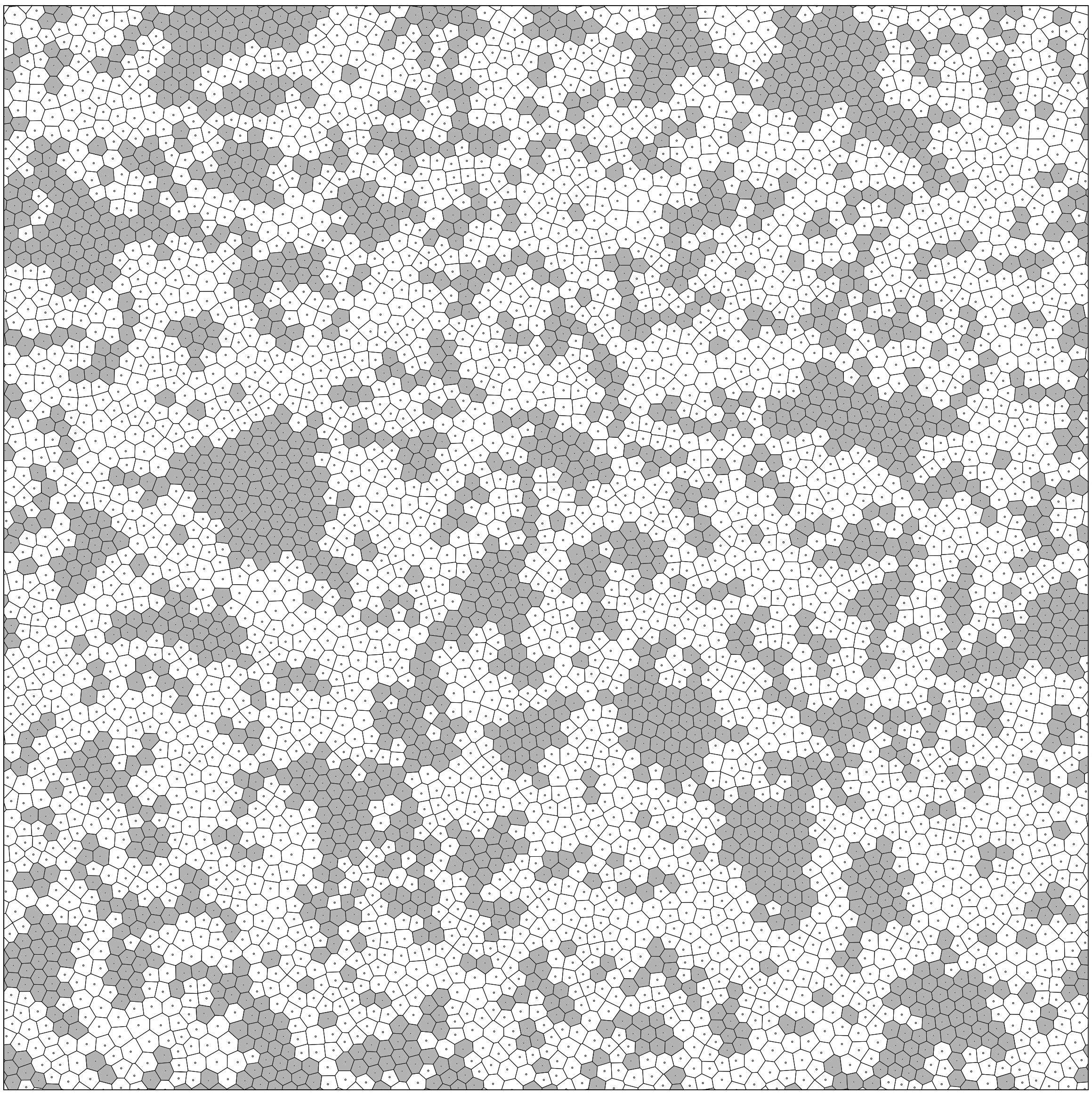
Identification of Clusters in 2D

- No rigorous definition.
- Solid-like particle has regular Voronoi hexagon in 2D.
- Characterize the "regularity" of each hexagon by the relative deviation of the lengths of its six edges:

$$t \equiv \sqrt{\frac{\langle l^2 \rangle - \langle l \rangle^2}{\langle l \rangle^2}}$$

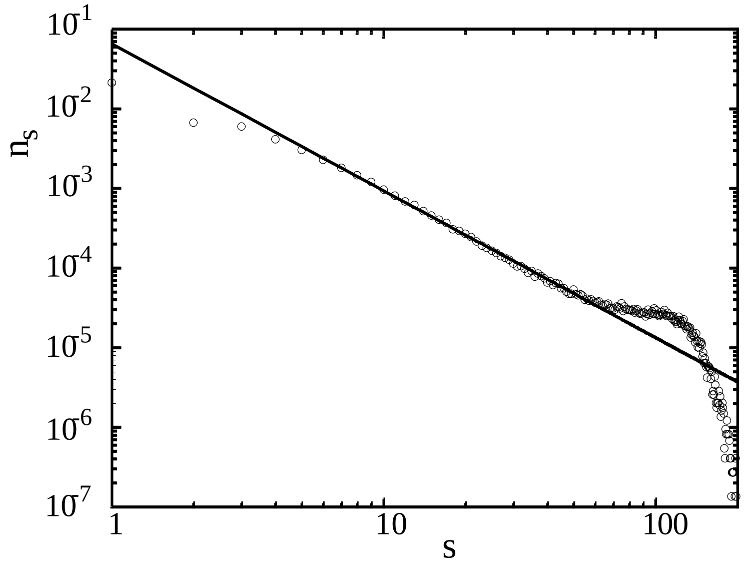
  A tetrahedron is regular if $t < t_c = 0.10$.
- Two "solid-like" particles that are neighbors belong to the same cluster.

$N = 5000,\ T = 3.3$

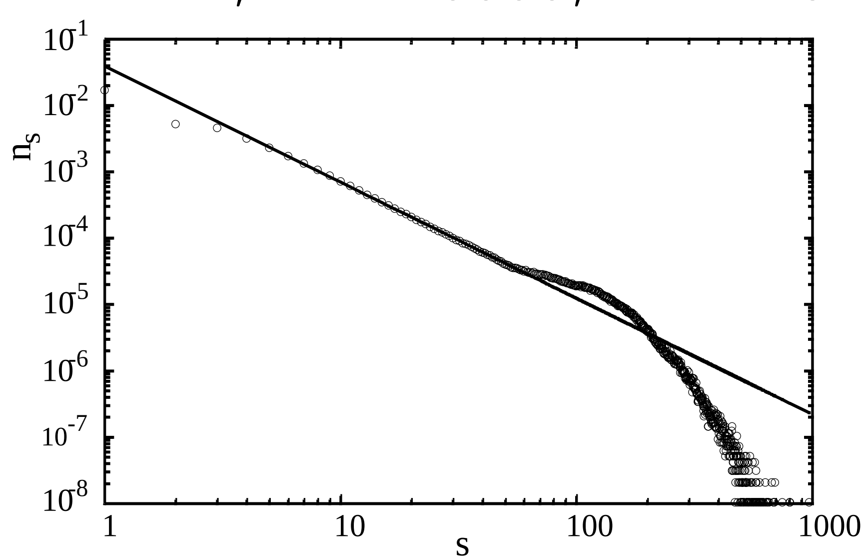


Cluster Size Distribution for 2D Lennard-Jones Mixture

$T = 3.3$, $N = 500$, $n_s \sim s^{-x}$, $x \approx 1.85$



$T = 2.7$, $N = 20000$, $x \approx 1.75$



Identification of Clusters in 3D

- An icosahedron is the structure that corresponds to hexagons in 2D, but icosahedra do not tile space, so become distorted.
- Tetrahedra (corresponding to triangles in 2D) work better.
- A group of four particles forms a tetrahedron if each is a neighbor of the other three.
- Characterize the "regularity" of each tetrahedron by the relative deviation of the lengths of the six edges of the tetrahedron:

$$t \equiv \sqrt{\frac{\langle l^2 \rangle - \langle l \rangle^2}{\langle l \rangle^2}}$$

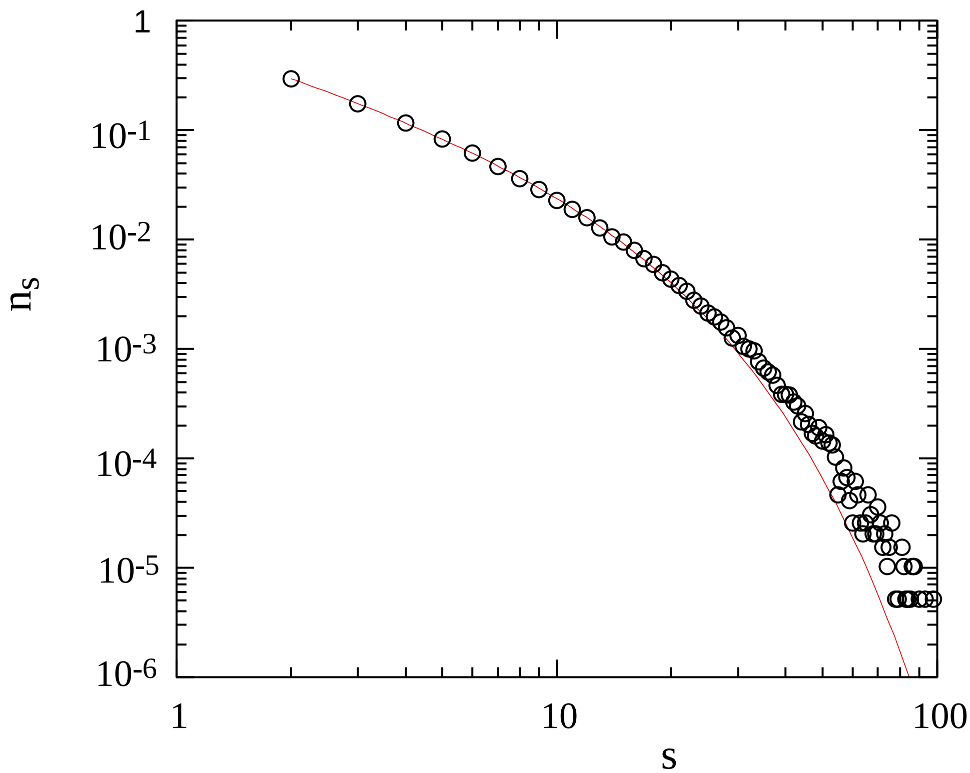
  A tetrahedron is regular if $t < t_c = 0.09$.

- Each particle is a member of multiple tetrahedra. If a particle is a member of n_c or more regular tetrahedra, the particle is considered "*solid-like*." Take $n_c = 10$.

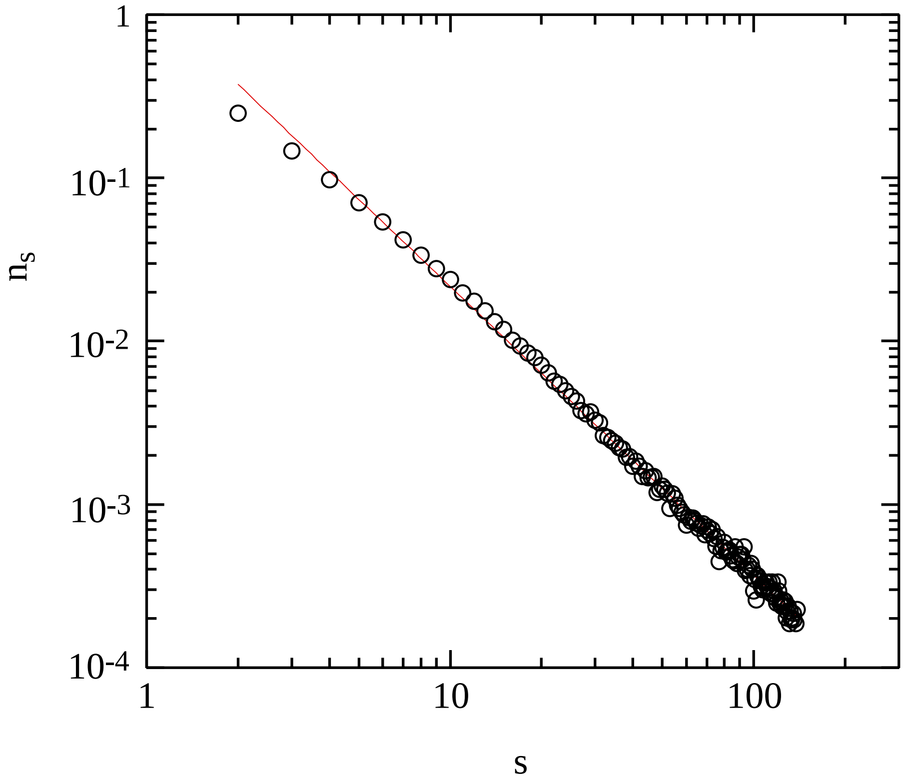
Cluster Size Distribution for 3D Kob-Andersen Interaction

$$T_{\text{mode coupling}} = 0.435$$

$T = 0.70$, $n_s \sim s^{-x} e^{-s/m_s}$, $x = 1.1$, $m_s = 9.5$.

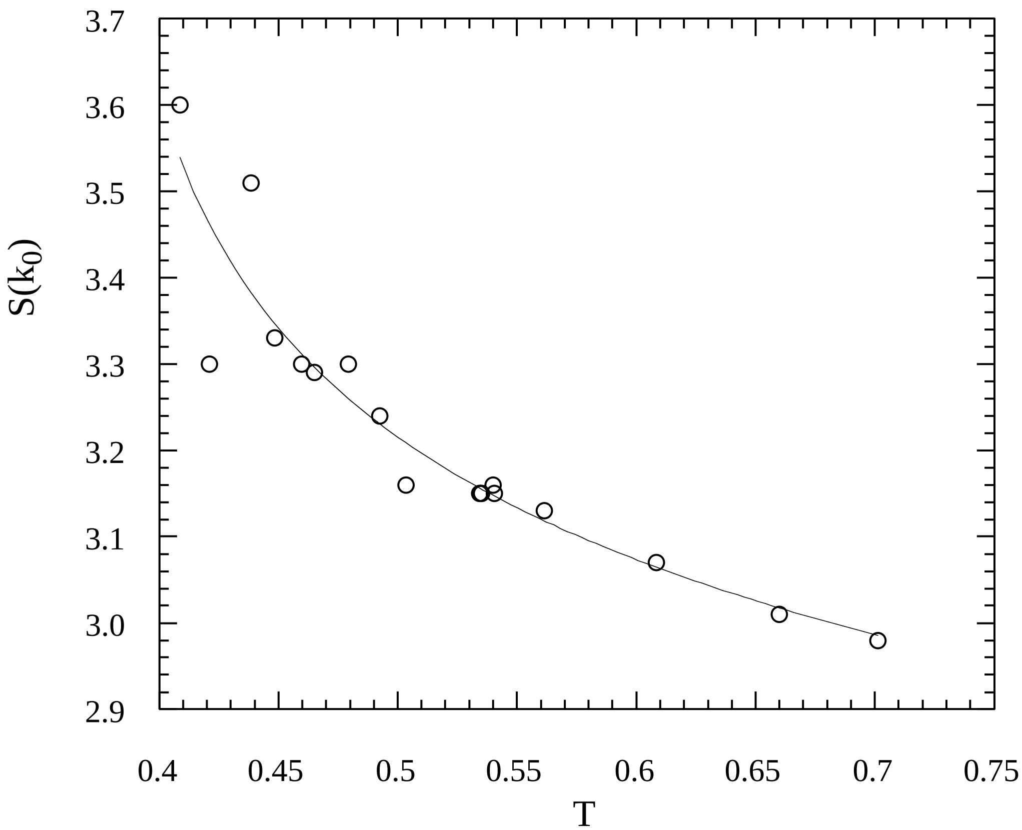


$T = 0.46$, $n_s \sim s^{-x}$, $x = 1.77$



Anghel, Klein, Rundle, and S'a Martins, "Scaling in a cellular automaton model of earthquake faults," cond-mat/0002459. Scaling of earthquake events in models of faults with long-range stress transfer consists of at least three distinct regions corresponding to three classes of earthquakes with different physical mechanisms. The structure and dynamics of earthquake events is identical to the structure and dynamics of fluctuations near spinodals and decompose scaling plot into a superposition of different power laws.

Apparent Divergence of peak of $S(k)$ in 3D



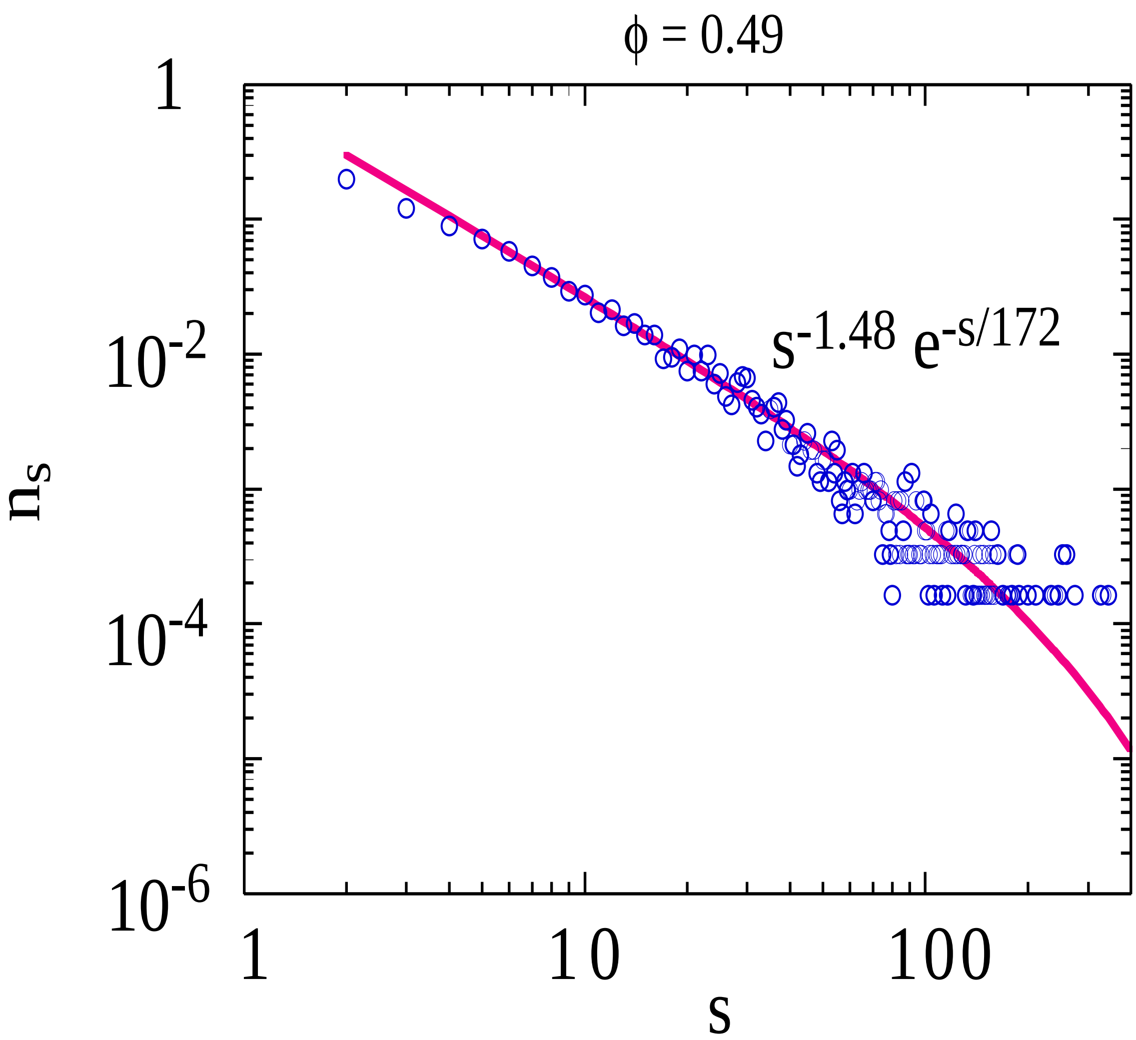
Prediction: $S(k_0) \sim \log(T - T_0)$ or no divergence.

Cannot distinguish between a power-law fit
$S(k_0) \sim (T - 0.37)^{-0.08}$ or
$S(k_0) \sim \log(T - 0.38) + \text{constant}$

Cluster Size Distribution for Hard Sphere Colloidal Glass

$$\phi_g = 0.58 \pm 0.01$$

Positions imaged by confocal microscopy.



Summary

Results that support pseudospinodal interpretation:

1. Cluster scaling consistent with theoretical predictions of mean-field critical behavior and arrested spinodal nucleation.

2. Identification of diverging length in 2D Lennard-Jones system.

3. Weak divergence of $S(k_0)$ in 3D Lennard-Jones systems.

Unanswered questions

1. Identification of divergent length in 3D systems.

2. Direct determination of cluster lifetime.

3. Explanation of Nagel-scaling for $\epsilon''(\omega)$.

L. L. Goncalves, M. Lopez de Haro, J. Taguena-Martinez, and R. B. Stinchcombe, "Nagel scaling, relaxation and universality in the kinetic Ising model in an alternating isotopic chain," *Phys. Rev. Lett.* **84**, 1507–1510 (2000), cond-mat/9911225.