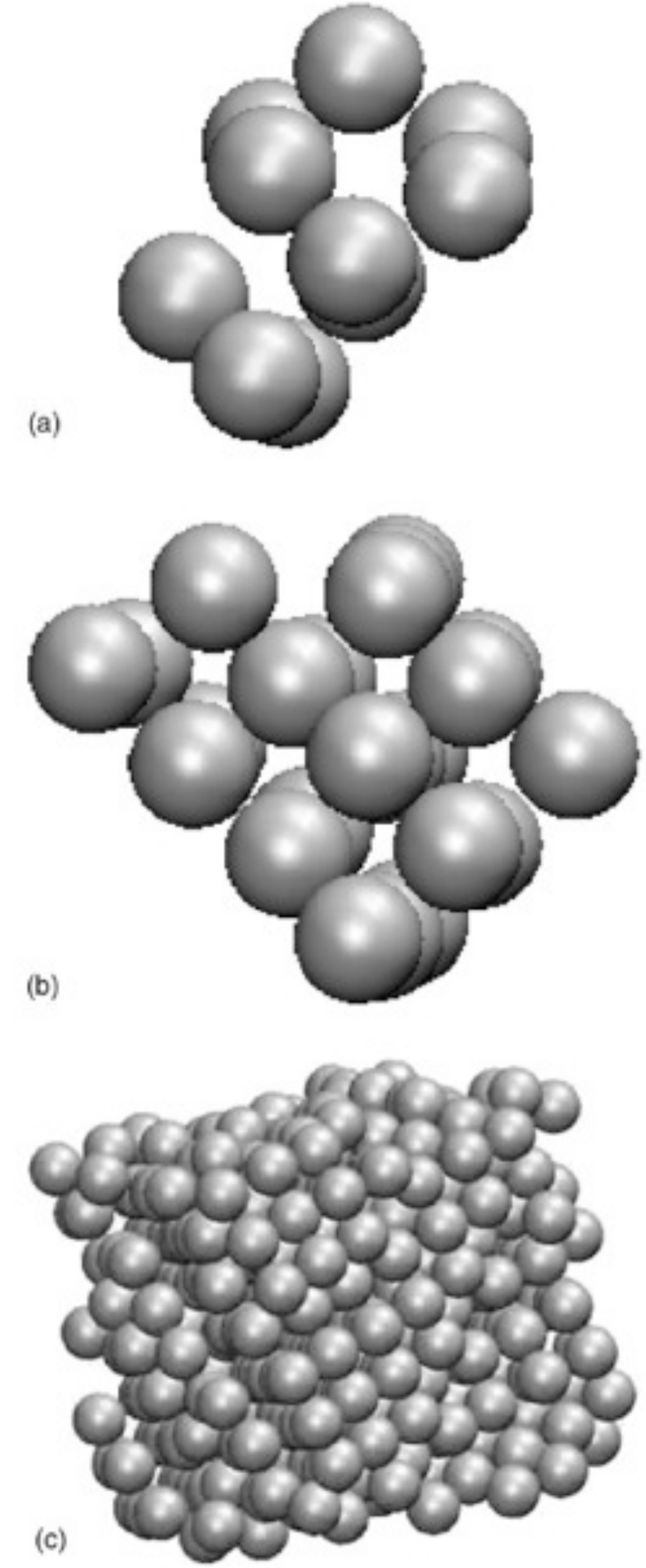
Lecture 1
Glass formation and crystal nucleation in supercooled liquids: insights from simulations

Peter H. Poole
St. Francis Xavier University
Antigonish, Nova Scotia, Canada

School on Glass Formers and Glasses - Bengaluru - January, 2010

Outline

- Timescales for liquid relaxation and for crystal nucleation.
- Methods: Evaluating crystal nucleation barriers and rates in simulations of supercooled liquids
- Biased sampling applied to nucleation (Frenkel and coworkers)
- “Mean first passage time” analysis (Reguera and coworkers)
- Illustrations from the literature and simple 2D Ising model demo.
- Role of structure and phase behaviour.



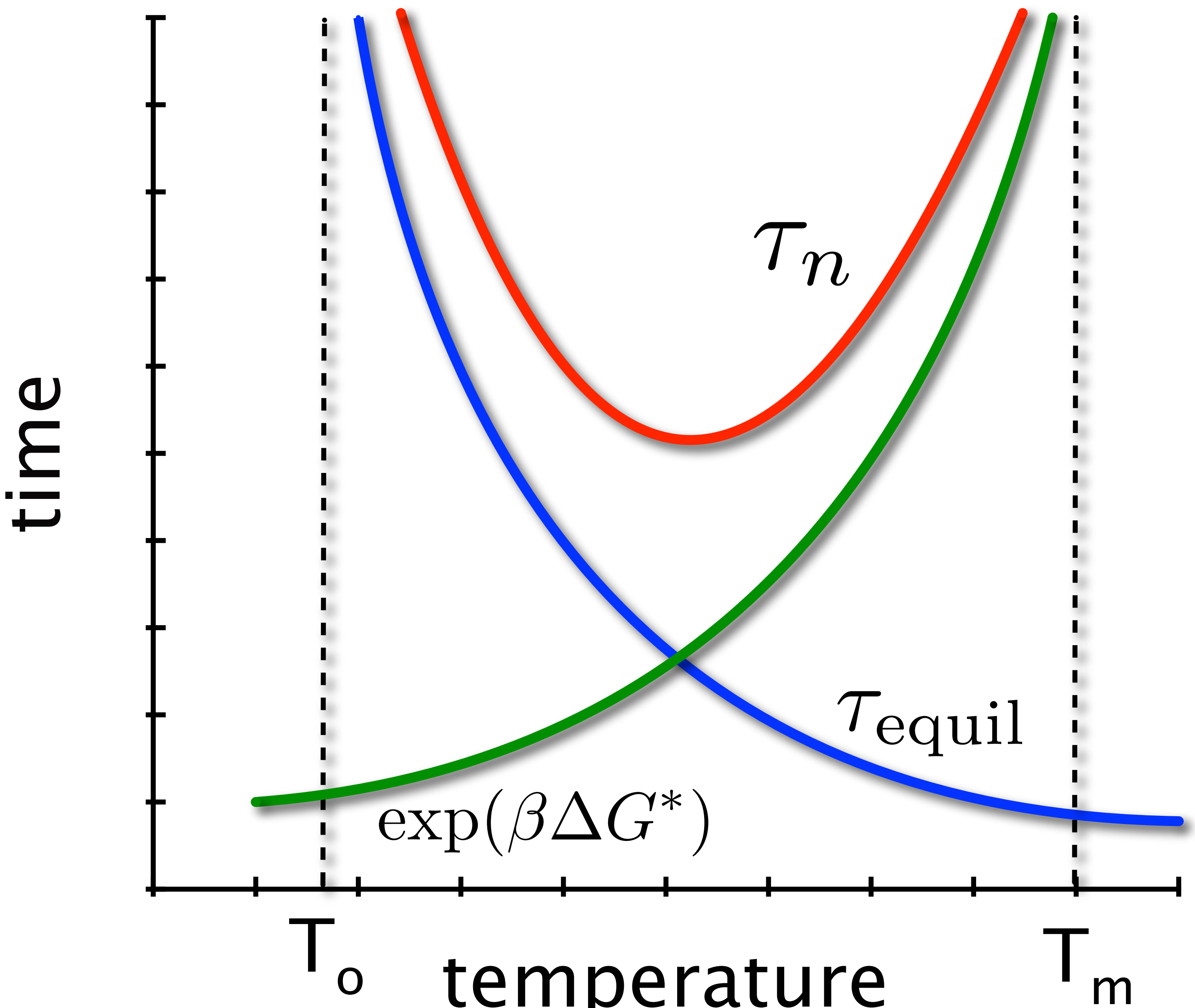
Motivations

- Efforts to form interesting new glassy materials (e.g. metallic glasses) are essentially efforts to avoid crystallization.

- Better understanding of the glass transition will require better understanding of crystallization, especially in deeply supercooled liquids. E.g. role of local order in both processes.

- Complex dynamics of glassy liquids can have a significant influence on the crystallization process. E.g. Stokes-Einstein decoupling.

Thermodynamic and dynamic contributions to the nucleation time



- In CNT, the nucleation time is

$$\tau_n = \frac{1}{JV} = K^{-1}\exp(\beta\Delta G^*)$$

- $K = \rho_n Z f_c^+$ is the kinetic prefactor.
- ρ_n is the number density of the particles.
- Z is the Zeldovich factor:

$$Z = \sqrt{\frac{\beta|\Delta\mu|}{6\pi n^*}} = \sqrt{\frac{\beta|G''(n^*)|}{2\pi}}$$

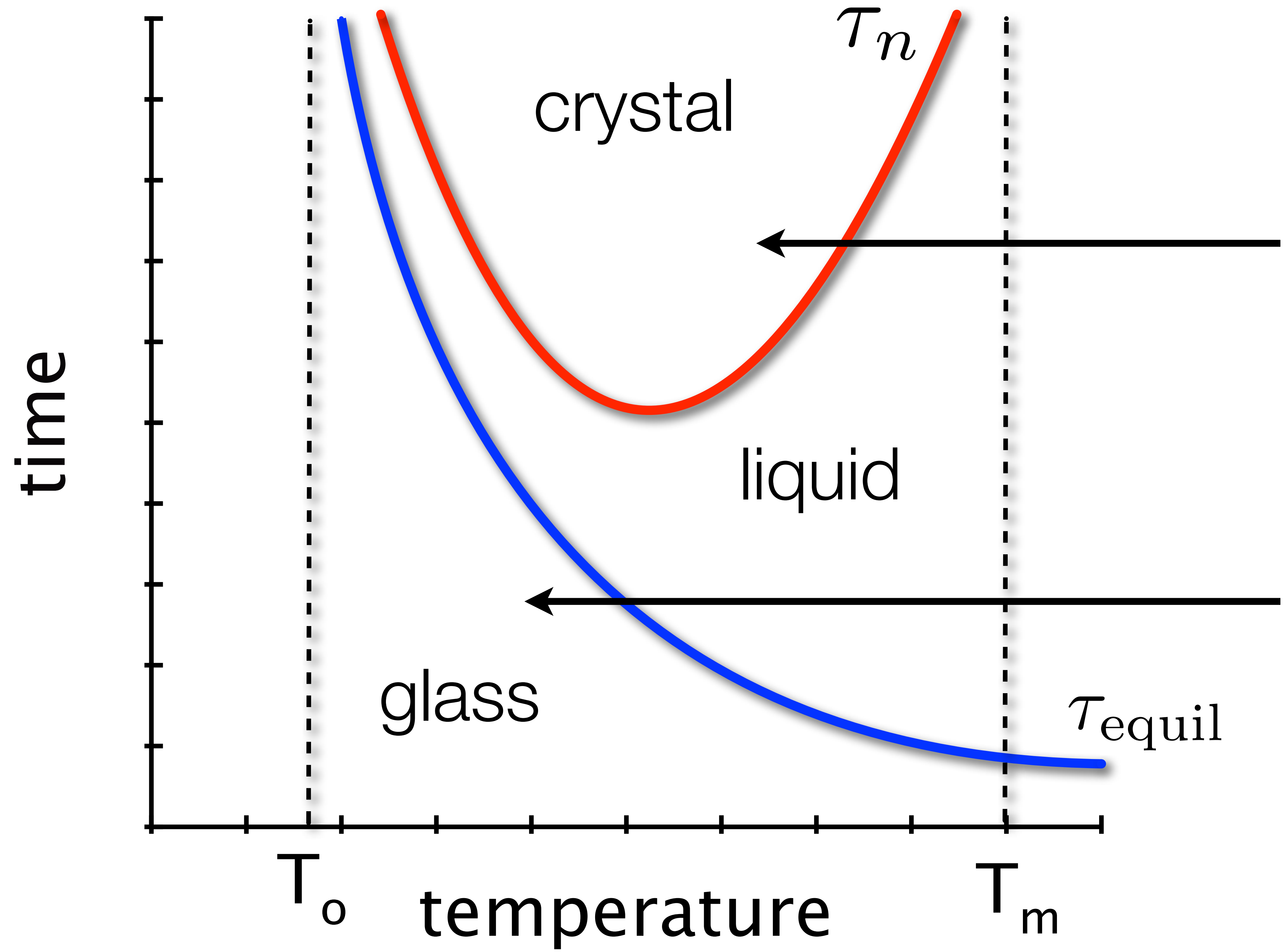
- f_c^+ is the attachment rate of particles to the critical nucleus, given by,

$$f_c^+ = \frac{24D(n^*)^{2/3}}{\lambda^2}$$

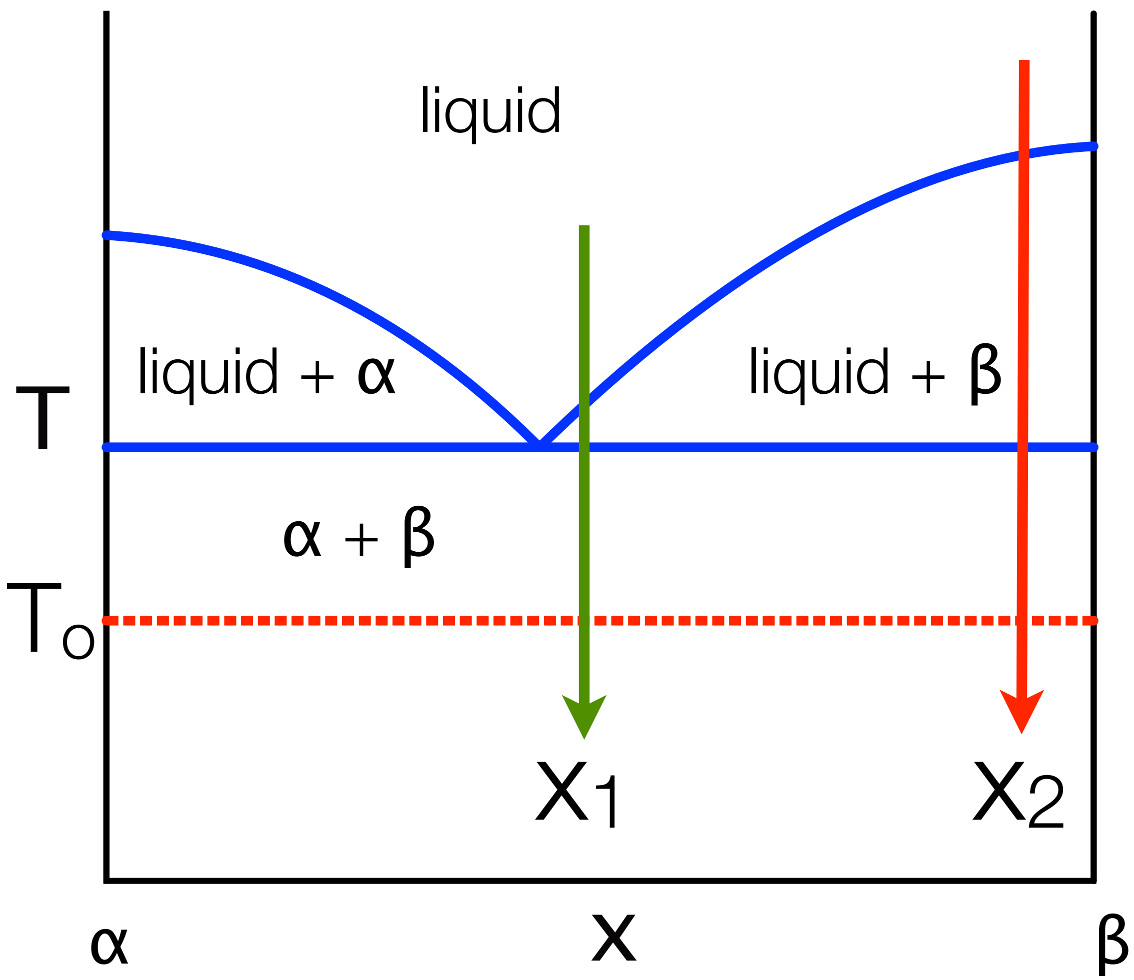
- So...

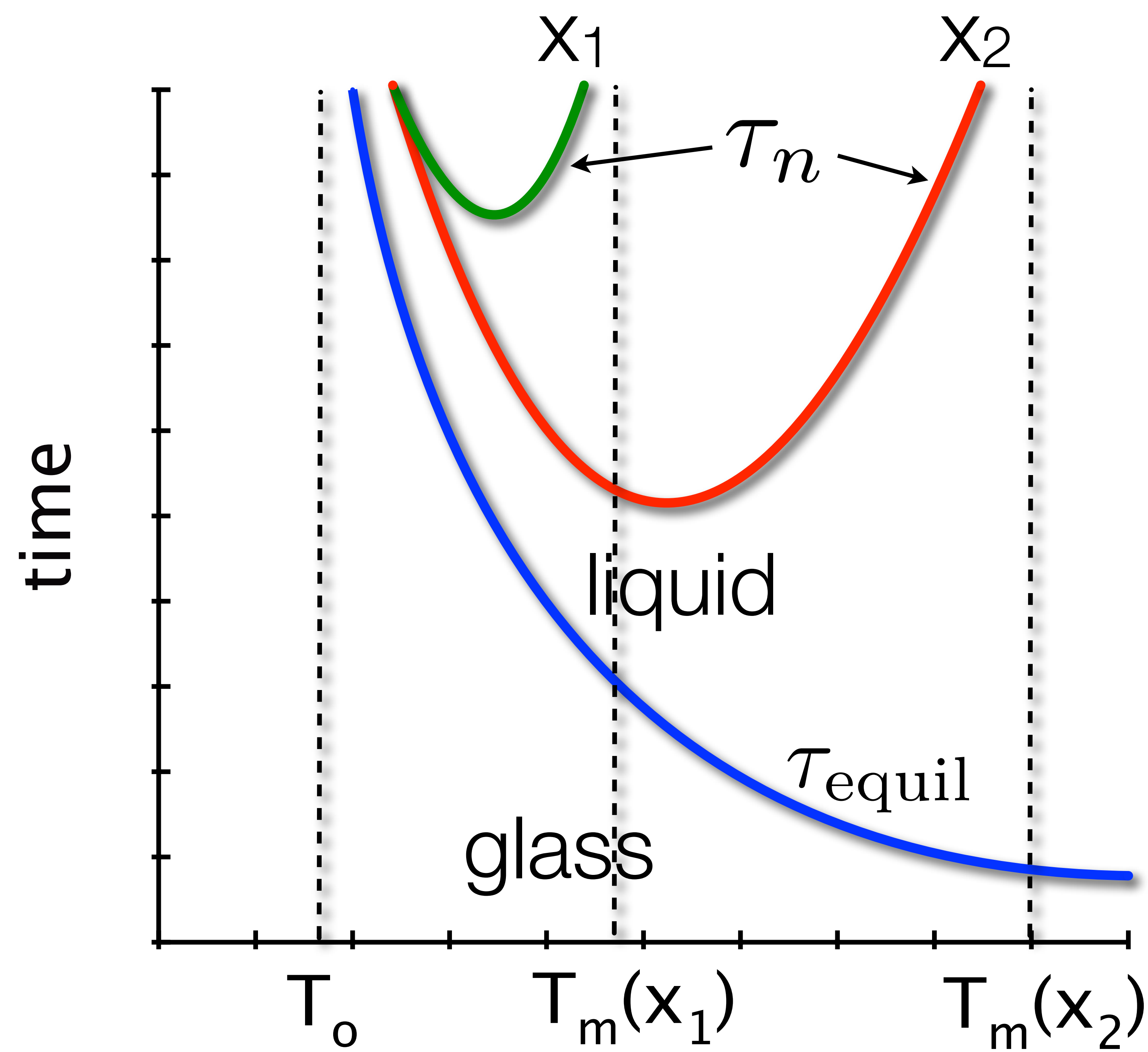
$$\tau_n = CD^{-1}\exp(\beta\Delta G^*)$$

Times and temperatures for accessing the liquid state



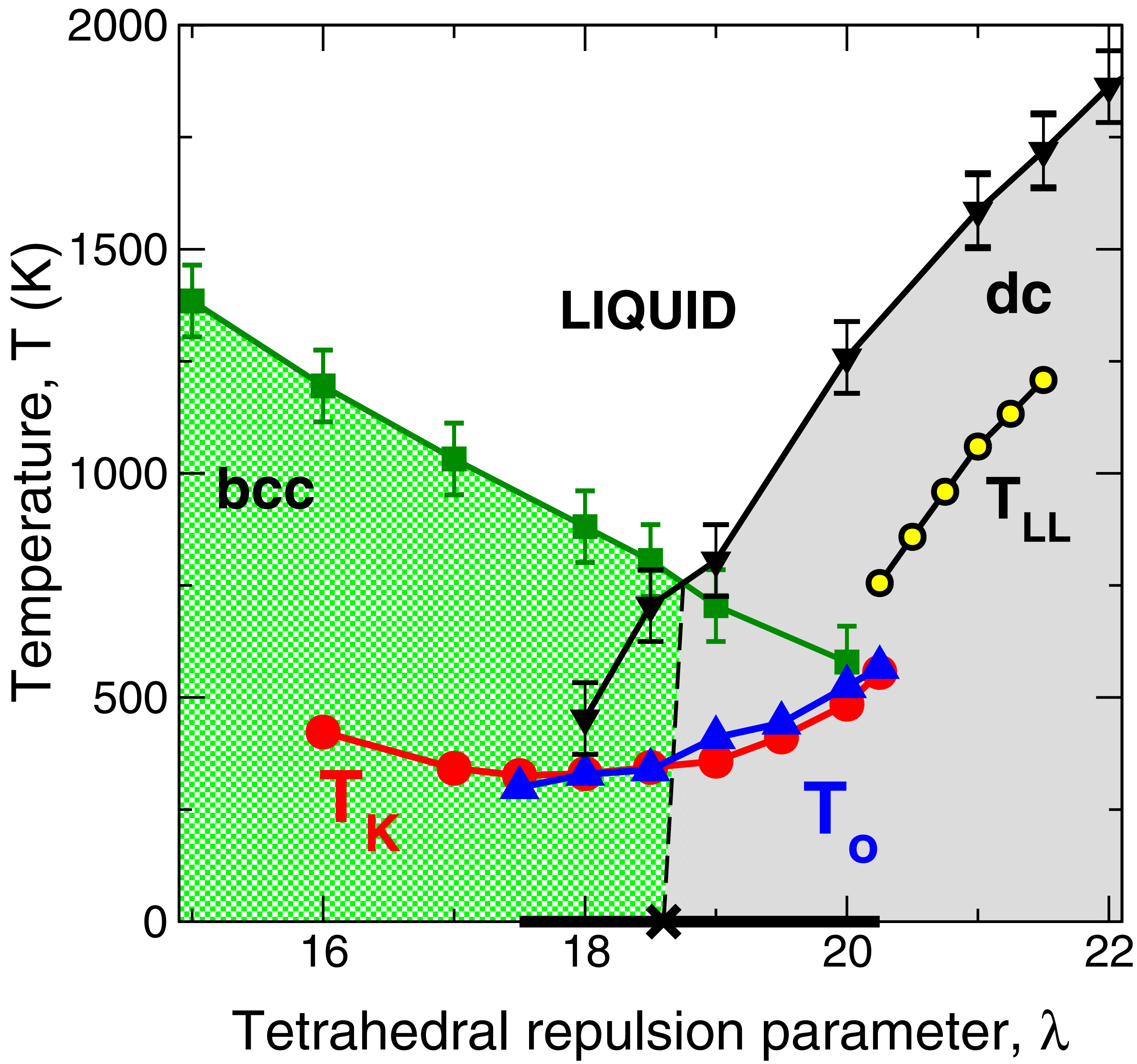
Phase behavior and glass-forming ability





Tuning of Tetrahedrality in a Silicon Potential Yields a Series of Monatomic (Metal-like) Glass Formers of Very High Fragility

Valeria Molinero,[1,*] Srikanth Sastry,[2] and C. Austen Angell[1]
[1]Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, USA
[2]Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur Campus, Bangalore, 560064, India

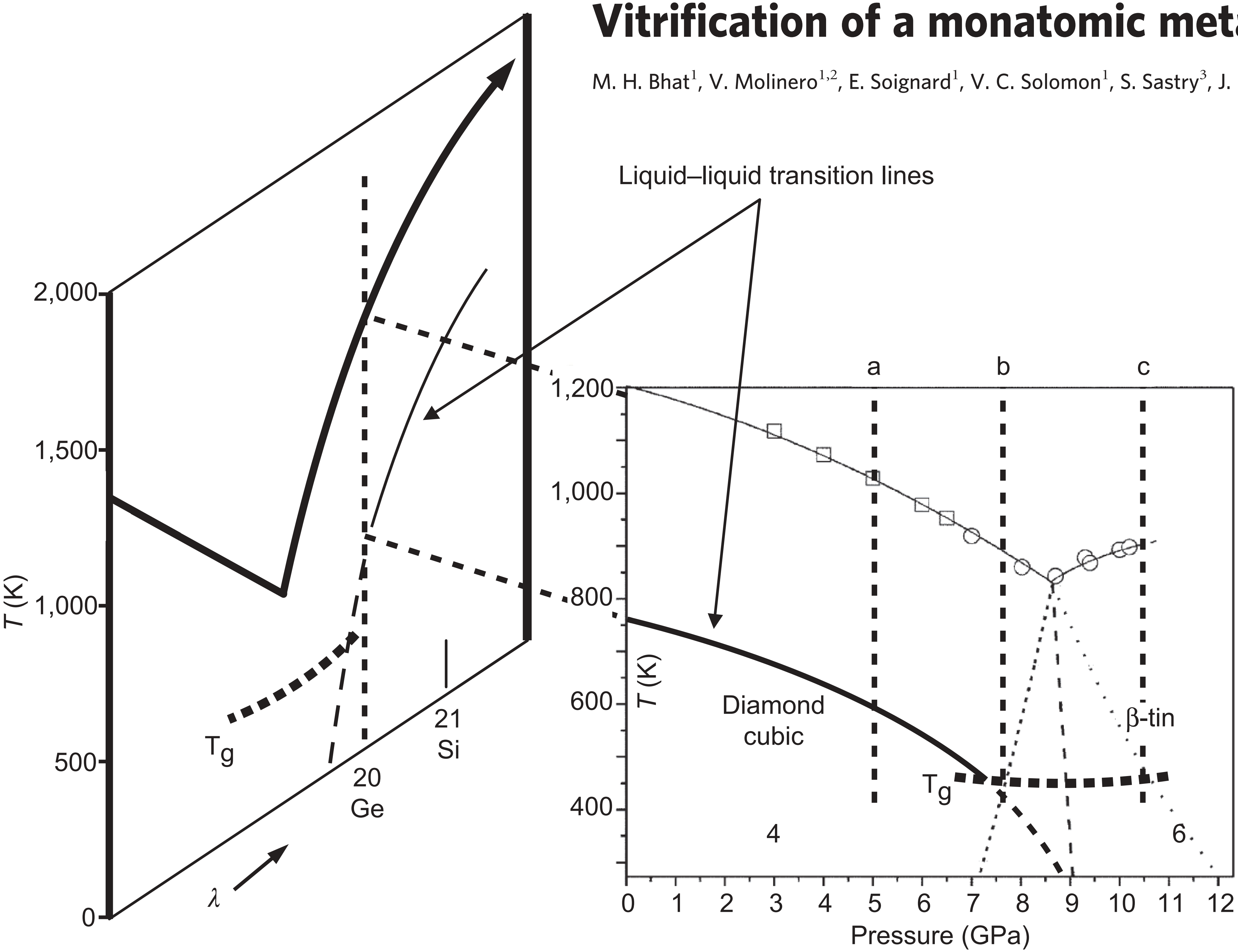


Vol 448|16 August 2007|doi:10.1038/nature06044 nature

LETTERS

Vitrification of a monatomic metallic liquid

M. H. Bhat[1], V. Molinero[1,2], E. Soignard[1], V. C. Solomon[1], S. Sastry[3], J. L. Yarger[1] & C. A. Angell[1]



Supercooling limits: a liquid spinodal?

PRL **101,** 256102 (2008) PHYSICAL REVIEW LETTERS week ending 19 DECEMBER 2008

Phase Transformation near the Classical Limit of Stability

Lutz Maibaum

Department of Chemistry, University of California, Berkeley, California 94720, USA

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

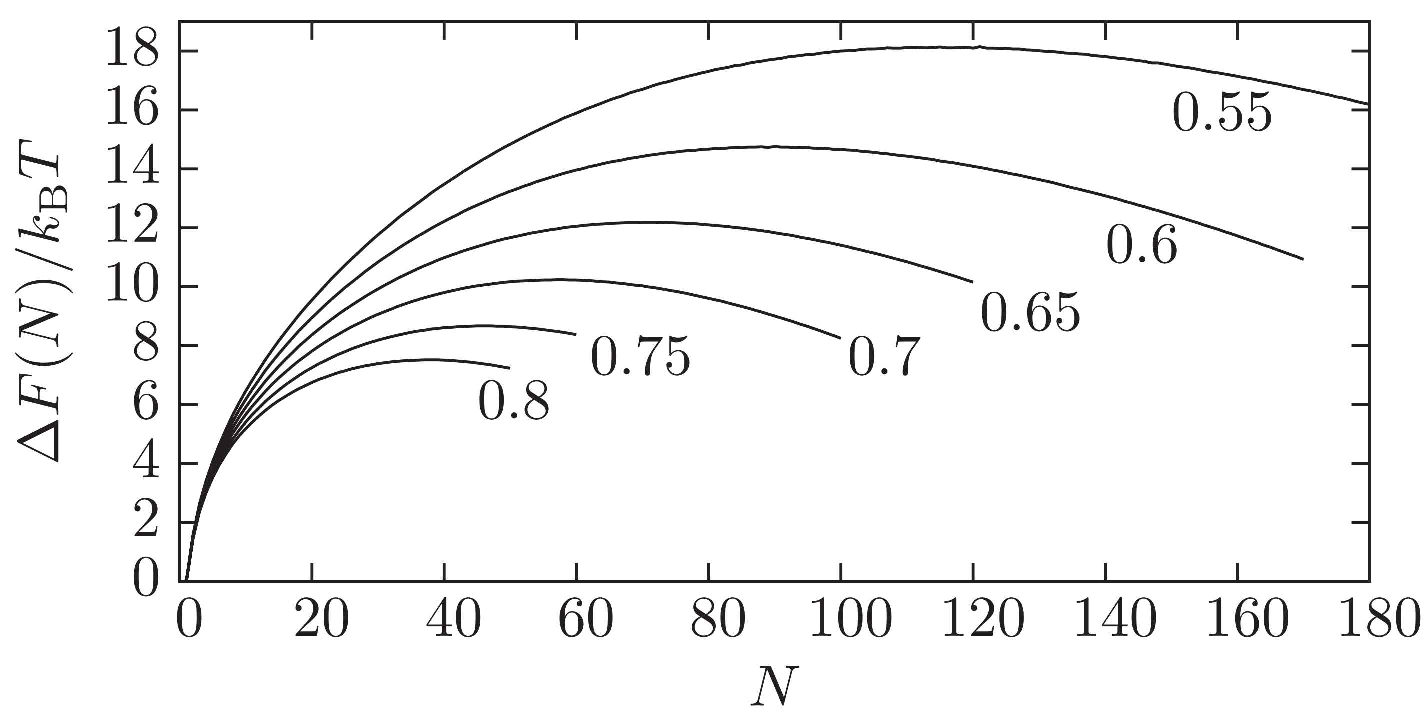
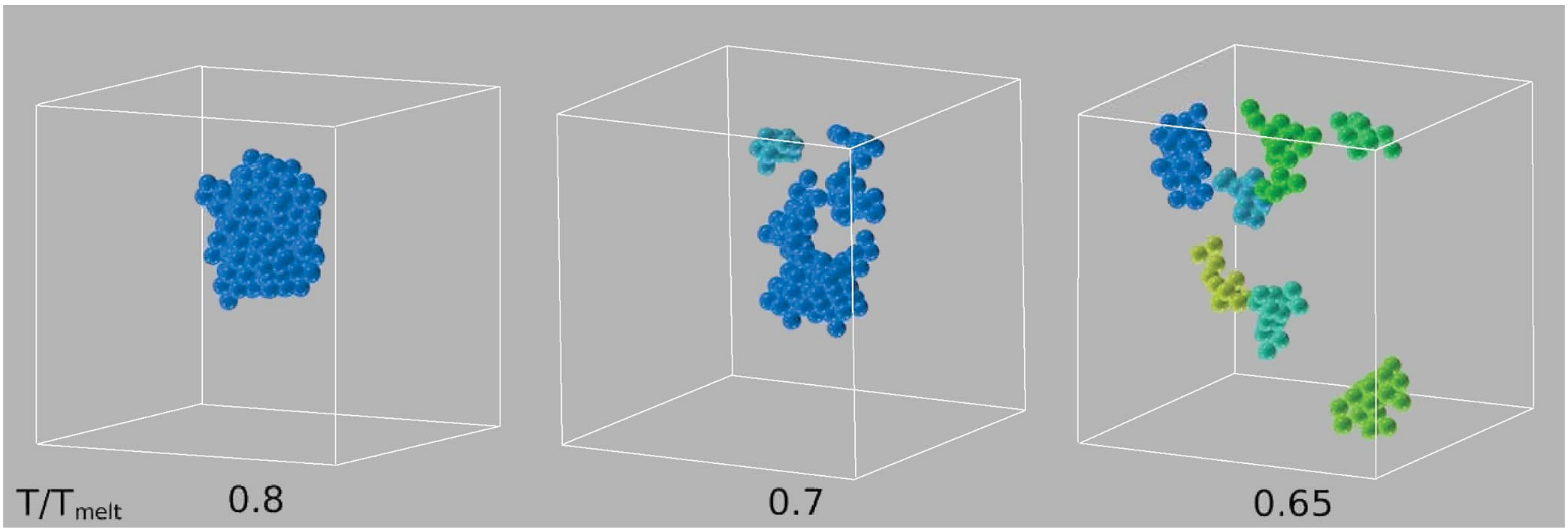


FIG. 1. Droplet free energy for various quench depths h/J as indicated in the figure. $\Delta F(N)$ has a single maximum at the critical nucleus size N_c and a corresponding activation barrier $\Delta F(N_c)$, which both decrease with increasing quench depth.

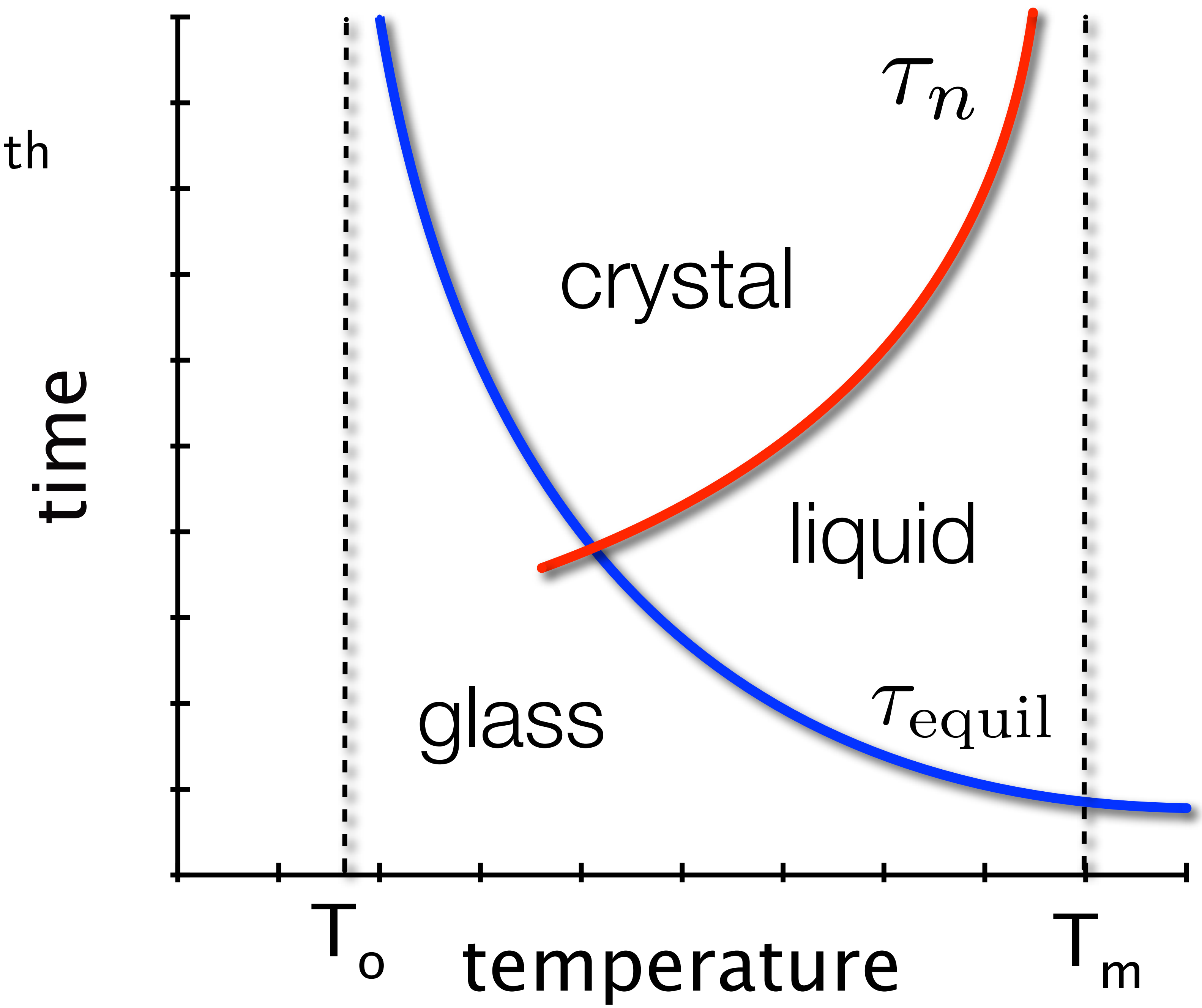
Freezing of a Lennard-Jones Fluid: From Nucleation to Spinodal Regime

Federica Trudu, Davide Donadio, and Michele Parrinello
ETH Zurich, Department of Chemistry and Applied Biosciences, c/o USI-Campus,
via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland
(Received 20 March 2006; published 6 September 2006)



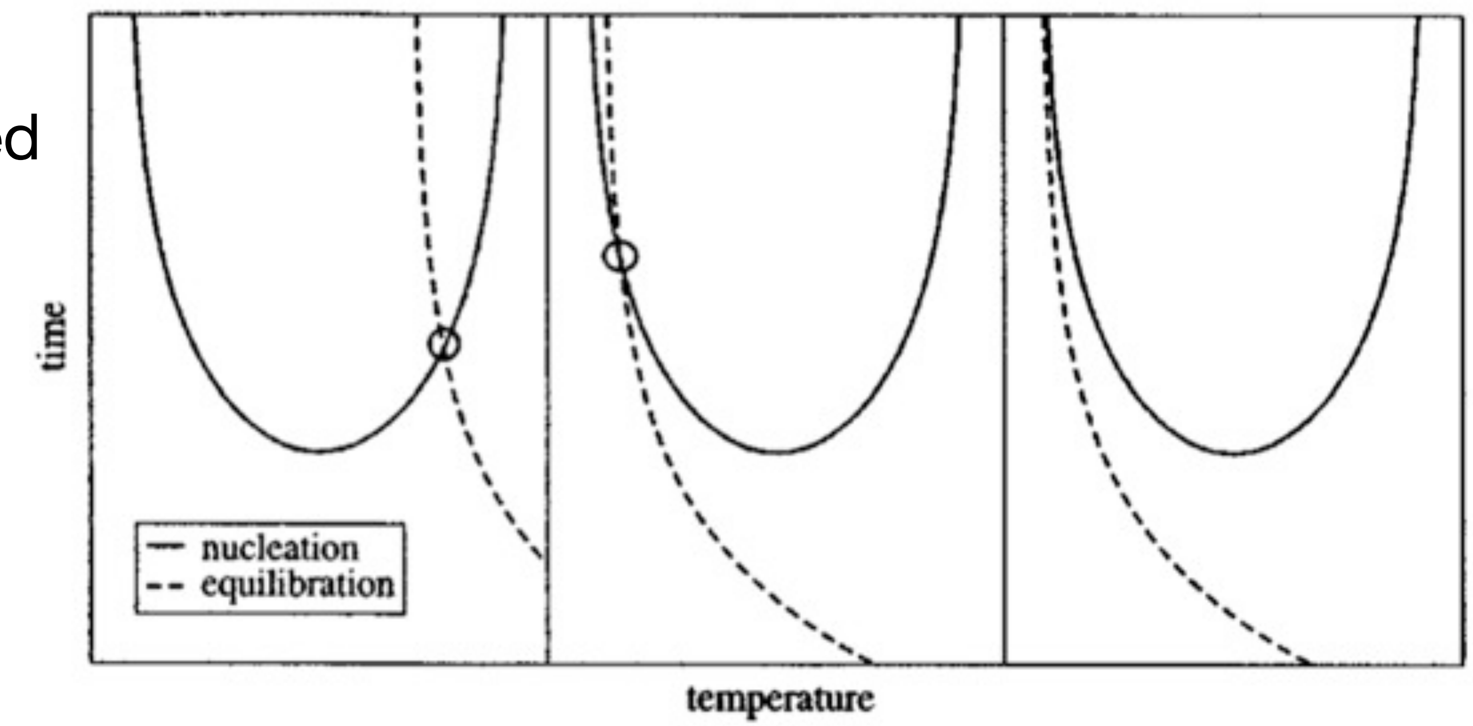
Supercooling limits: a "kinetic spinodal"?

- $\tau_n = CD^{-1} \exp(\beta \Delta G^*)$
- What if D^{-1} does not scale with τ_{equil} at low T, e.g. due to breakdown of Stokes-Einstein relation?
- Imposes a finite T limit for observing the liquid state...a "kinetic spinodal".



Recent work on stability limits of supercooled liquids...

- A. Cavagna and coworkers: “kinetic spinodal temperature” for supercooled liquids...
  - EPL 61, 74 (2003)
  - JCP 118, 6974 (2003)
  - PRL 95, 115702 (2005)



- Spinodal-like crystal nucleation in deeply supercooled LJ liquid...
  - Trudu, Donadio and Parrinello, PRL 97, 105701 (2006)
  - Wang, Gould and Klein, PRE 76, 031604 (2007)

- Stability limits for crystal nucleation in supercooled gold nanoclusters...
  - Mendez-Villuendas, Saika-Voivod and Bowles, JCP, 127, 154703 (2007)

Kauzmann's Paradox

- A thermodynamic problem (the impending entropy catastrophe of supercooled liquids) is not resolved by appealing to a dynamic phenomenon (the glass transition).
- Kauzmann's own solution: Crystallization becomes unavoidable on deep supercooling.

THE NATURE OF THE GLASSY STATE AND THE BEHAVIOR OF LIQUIDS AT LOW TEMPERATURES

WALTER KAUZMANN
Department of Chemistry, Princeton University, Princeton, New Jersey

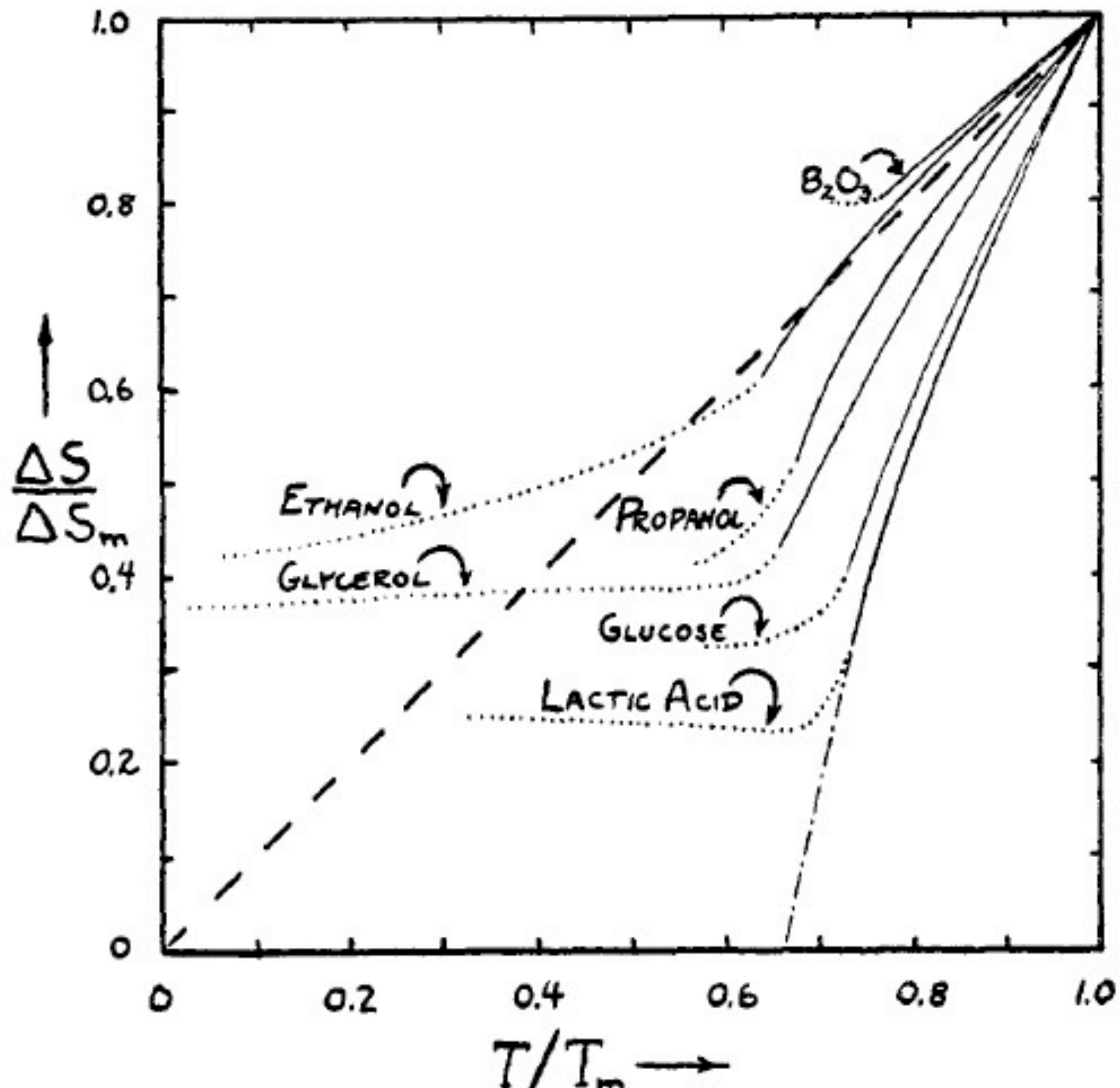
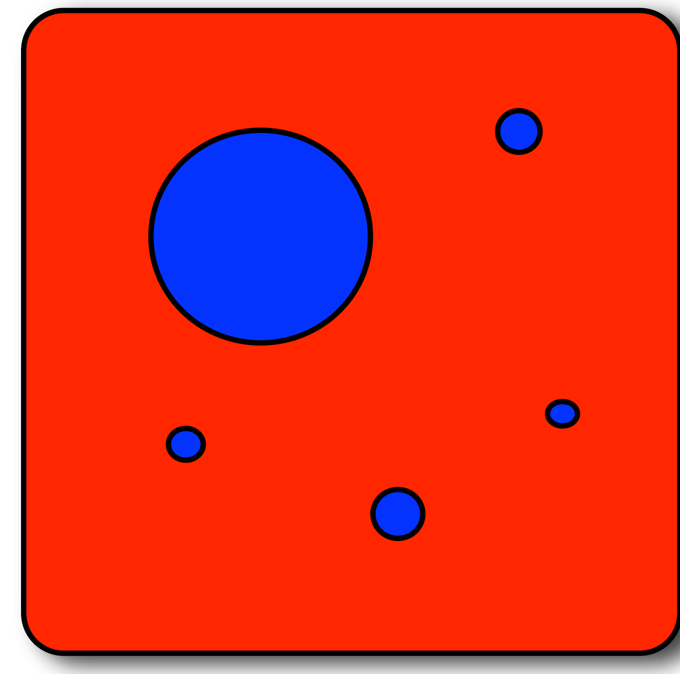


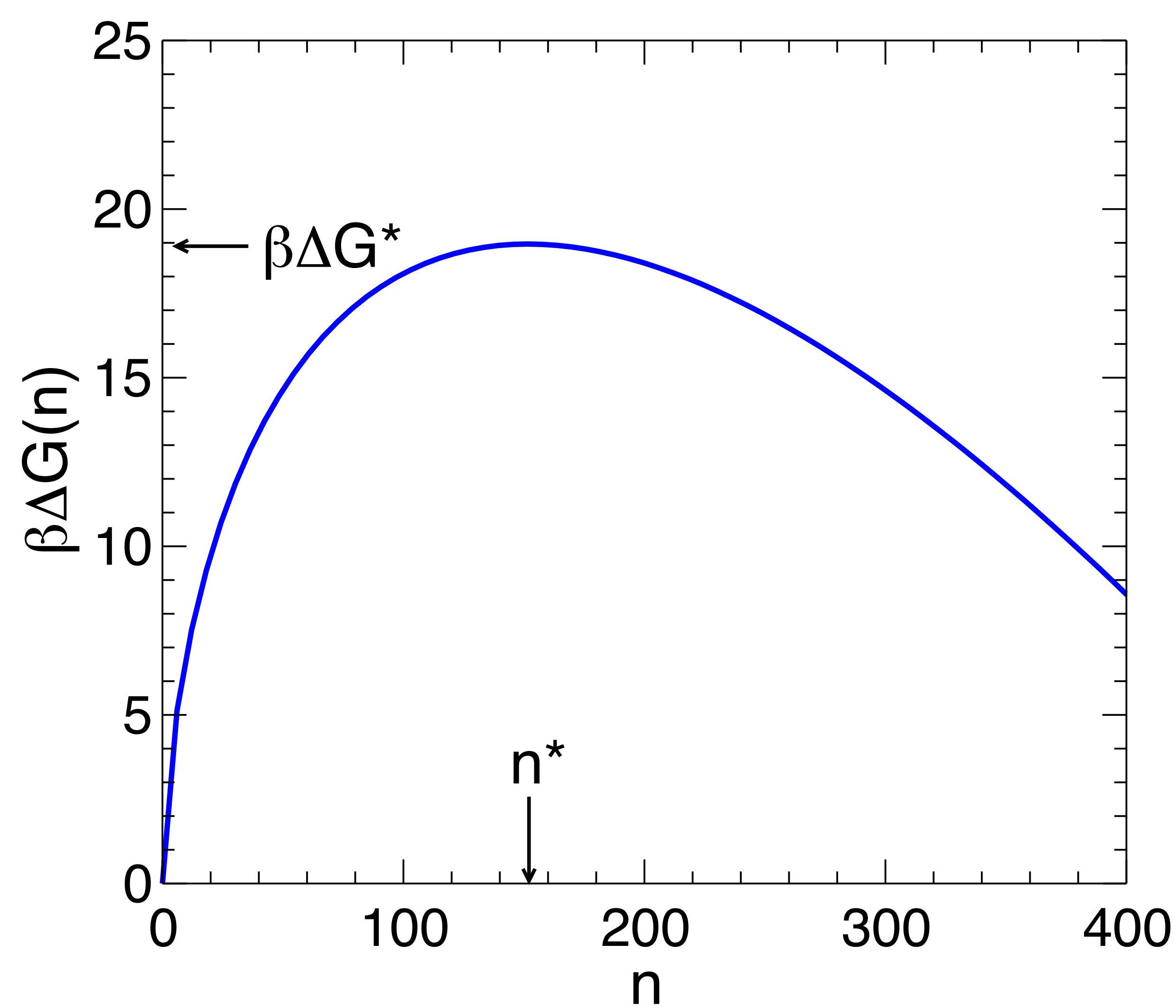
FIG. 4. Differences in entropy between the supercooled liquid and crystalline phases. Abscissa: as in figure 3. Ordinate: difference in entropy expressed as fraction of the entropy of fusion.

W. Kauzmann, Chem. Rev. 43, 219 (1948)

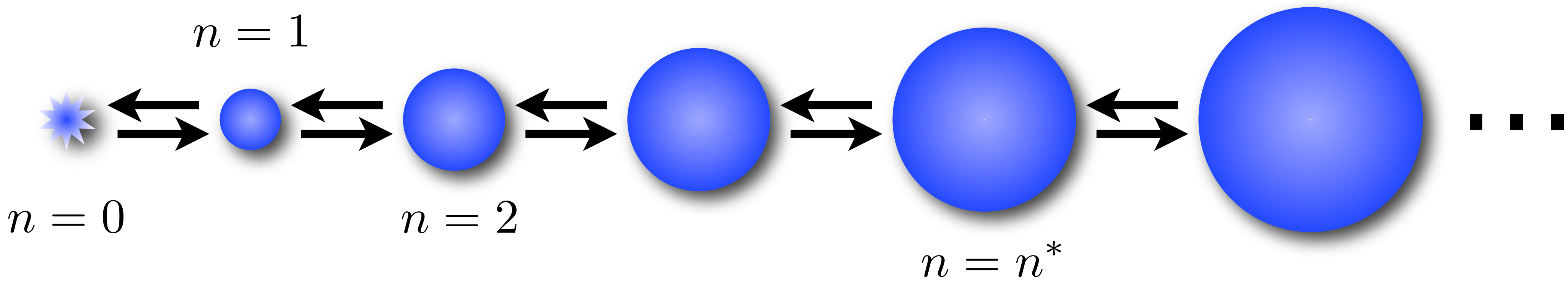
Classical nucleation theory (CNT)

- In CNT the nucleation rate is given by
  $J = K \exp\left(-\beta\Delta G^*\right)$
- $\Delta G(n)$ is the work to form a nucleus of the stable phase containing n particles.
- K is the kinetic prefactor.
- $\Delta G(n) = an^{2/3} - bn$
- ΔG^* is the height of the nucleation barrier.
- n^* is the number of particles in the critical nucleus.
- $\beta = 1/kT$

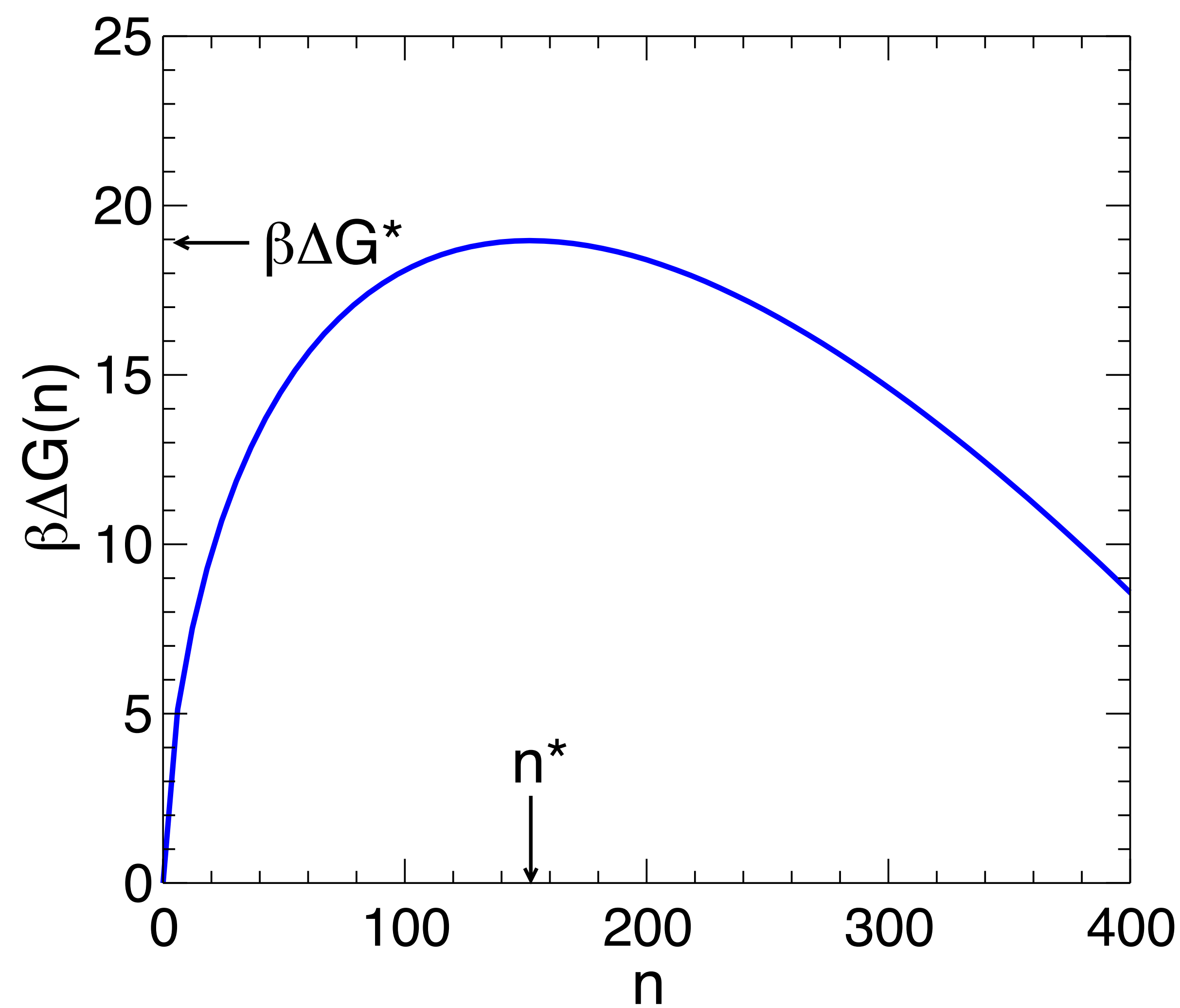




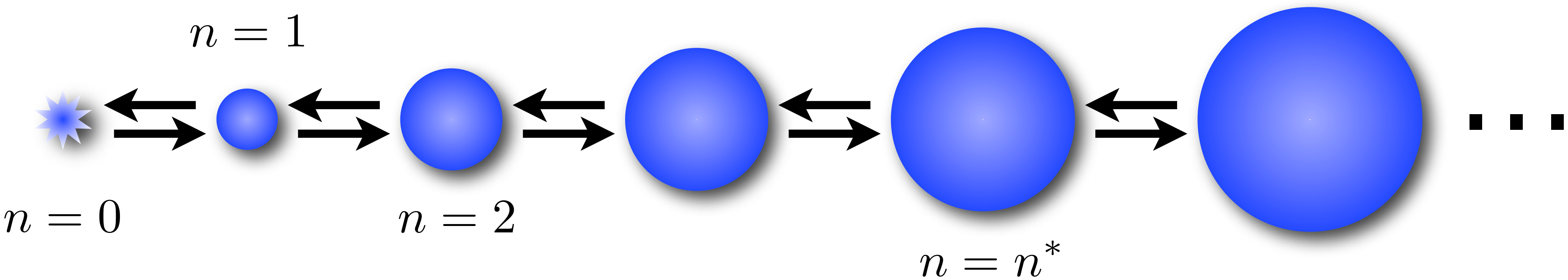
Classical nucleation theory (CNT)



- $\Delta G(n)$ is the work required to form a nucleus containing n particles.
- $\beta \Delta G(n) = -\log \frac{N(n)}{N_0}$
- $N(n)$ is the number density of clusters of size n.
- N_0 is the number density of the metastable phase.

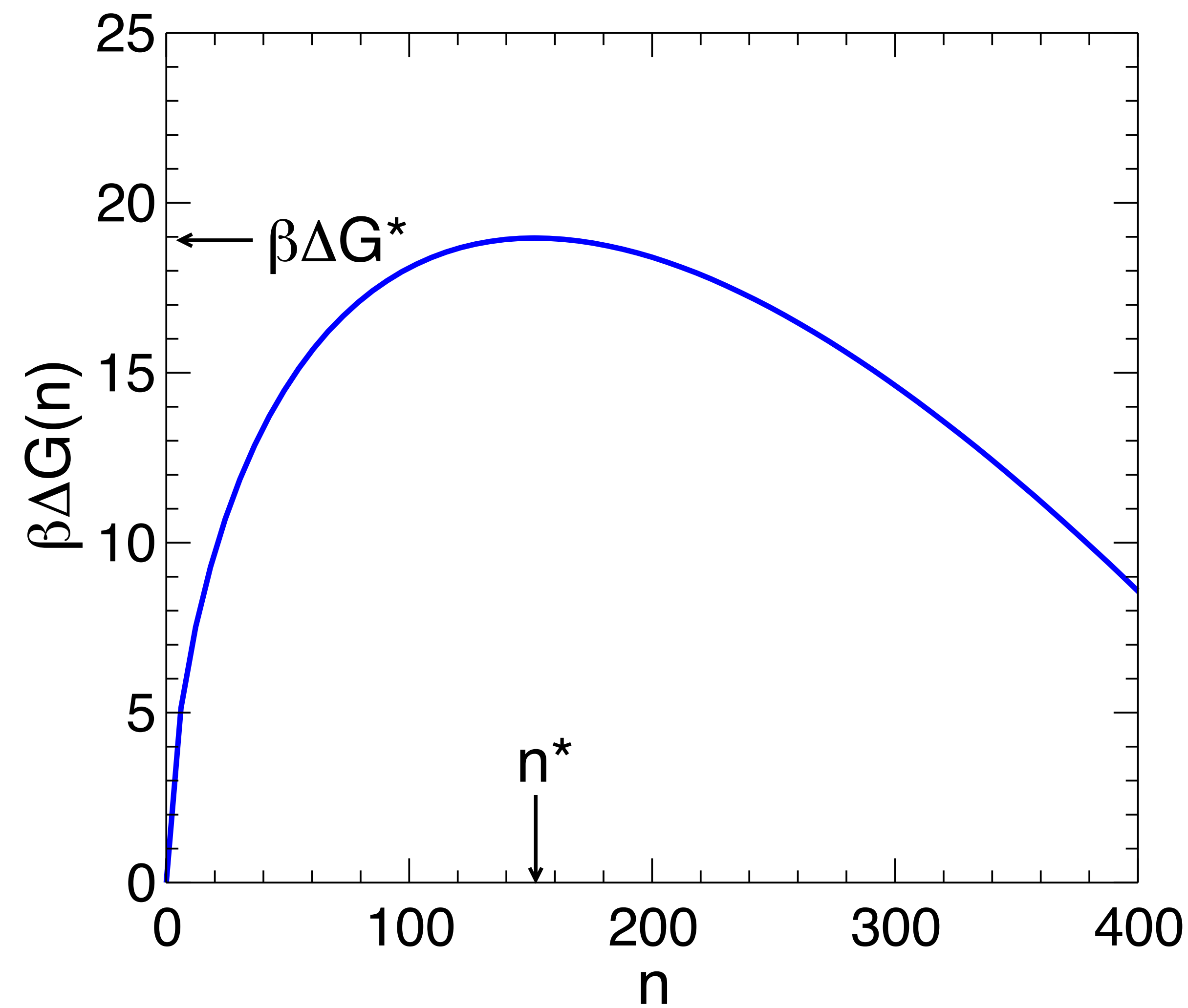


Classical nucleation theory (CNT)



Two challenges for finding $N(n)$ in simulations of crystal nucleation:

- Labelling particles as liquid-like or crystal-like. What's n?
- Sampling the equilibrium cluster distribution associated with a rare and irreversible process.



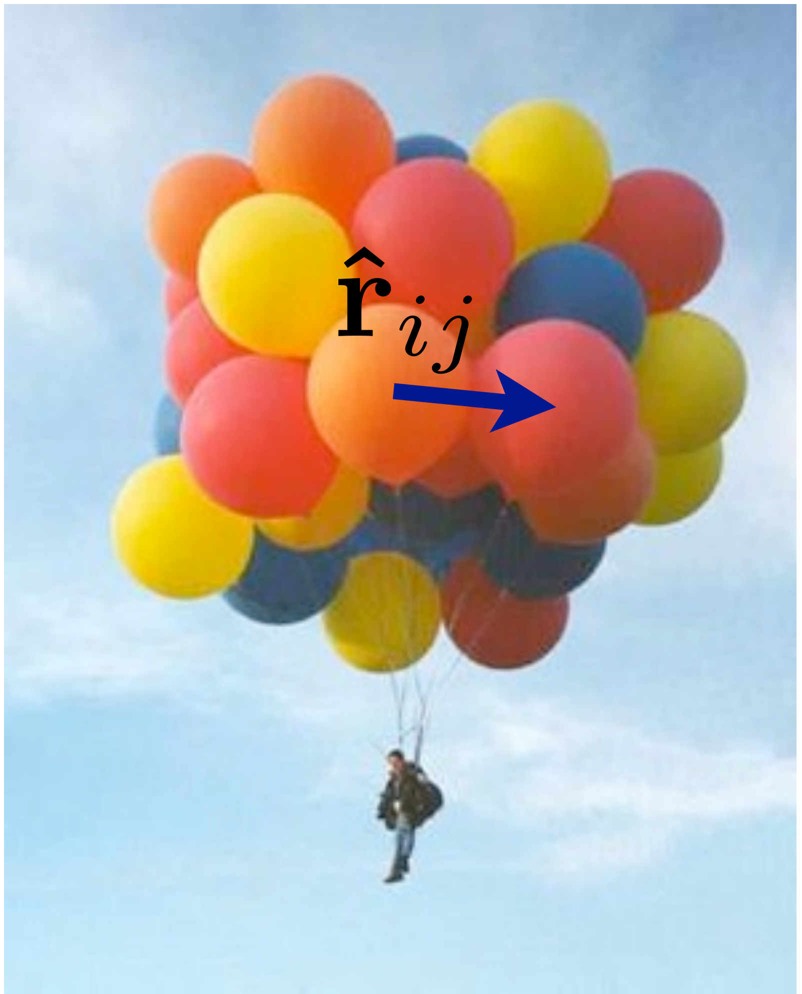
Identifying crystal-like particles in a supercooled liquid

- Frenkel and coworkers: Define a local orientational order parameter, based on spherical harmonics (Steinhardt).
- See: Ten Wolde, Ruiz-Montero and Frenkel, JCP, 1996; Faraday Discuss., 1996.

$$\bar{q}_{lm}(i) \equiv \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{ij})$$

l=6, m=3

l=6, m=4



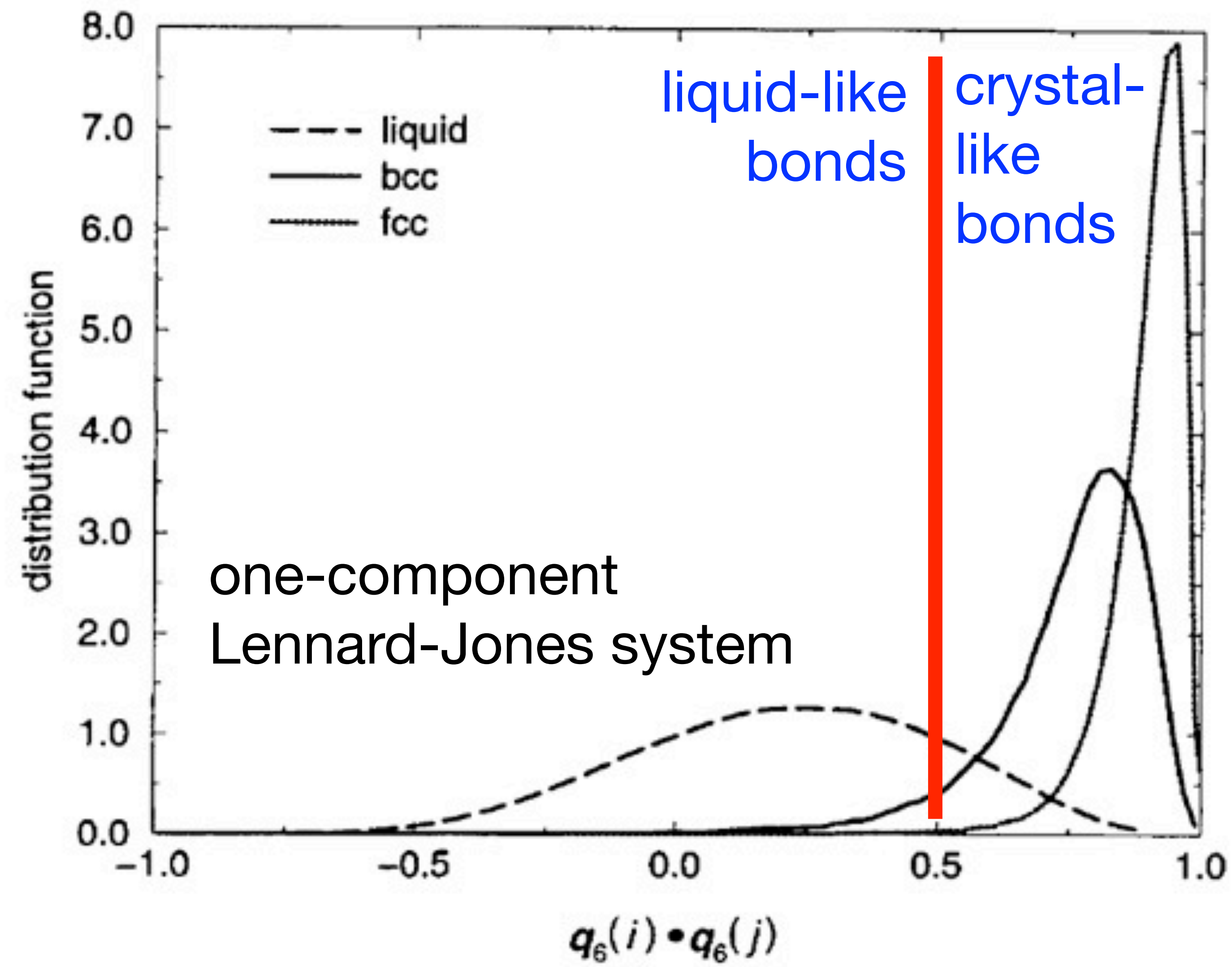
Identifying crystal-like particles in a supercooled liquid

- A crystalline bond exists between particles i and j when $\mathbf{q}_6(i) \cdot \mathbf{q}_6(j) > 0.5$

$$\bar{q}_{lm}(i) \equiv \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{ij})$$

$$\tilde{q}_{6m}(i) \equiv \frac{\bar{q}_{6m}(i)}{\left[\sum_{m=-6}^{6} |\bar{q}_{6m}(i)|^2\right]^{1/2}}$$

$$\mathbf{q}_6(i) \cdot \mathbf{q}_6(j) \equiv \sum_{m=-6}^{6} \tilde{q}_{6m}(i) \tilde{q}_{6m}(j)^*$$



ten Wolde, et al., Faraday Discuss., 1996

Identifying crystal-like particles in a supercooled liquid

A particle is defined to be a crystalline particle when it has 8 or more crystalline bonds with its nearest neighbours in the first coordination shell.

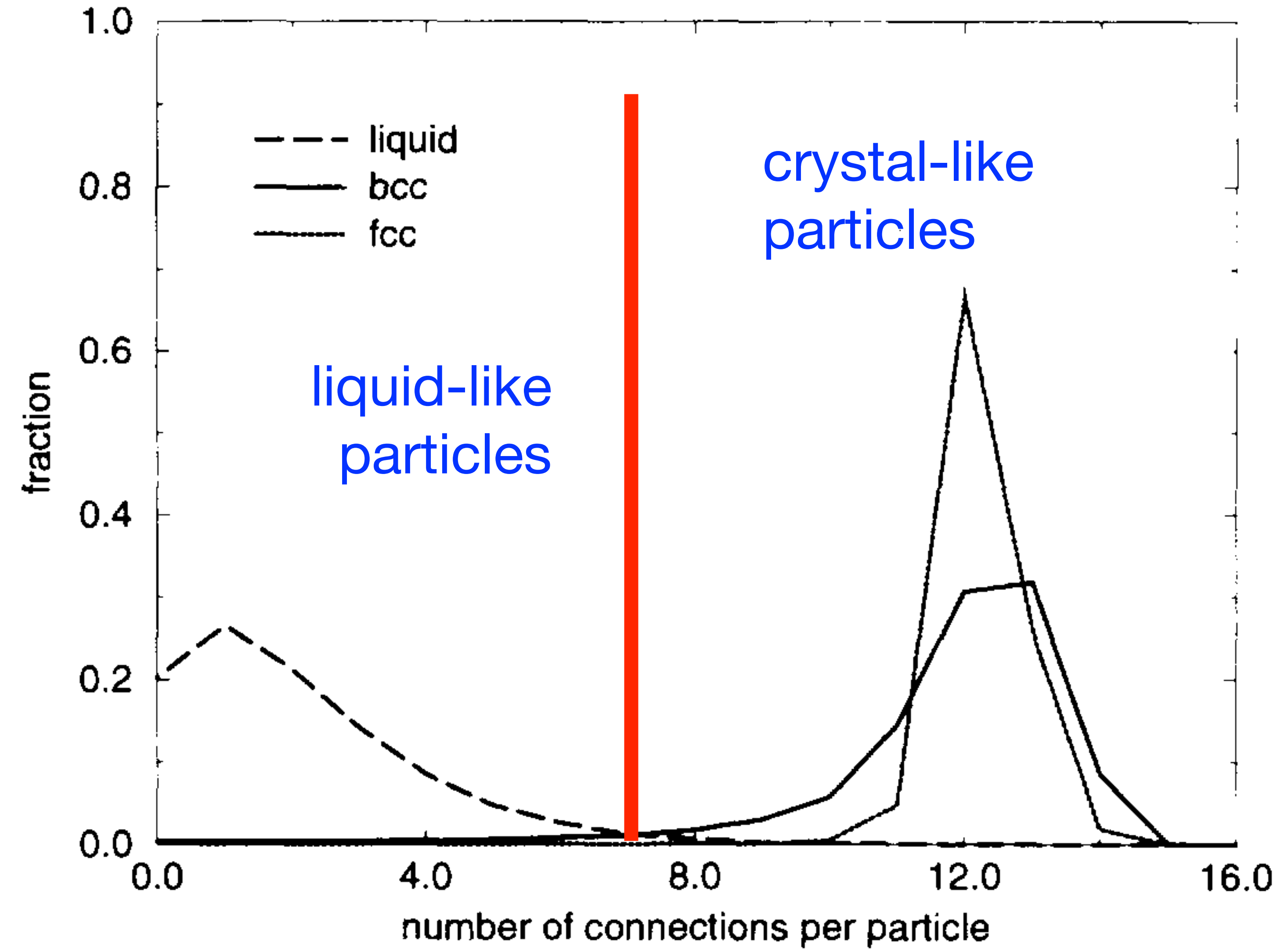
Liquid particles are those with 7 or fewer crystalline bonds with their nearest neighbours.

$$\bar{q}_{lm}(i) \equiv \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{ij})$$

$$\tilde{q}_{6m}(i) \equiv \frac{\bar{q}_{6m}(i)}{\left[\sum_{m=-6}^{6} |\bar{q}_{6m}(i)|^2\right]^{1/2}}$$

$$\mathbf{q}_6(i) \cdot \mathbf{q}_6(j) \equiv \sum_{m=-6}^{6} \tilde{q}_{6m}(i) \tilde{q}_{6m}(j)^*$$

one-component Lennard-Jones system



ten Wolde, et al., Faraday Discuss., 1996

Identifying crystal-like particles in a supercooled liquid

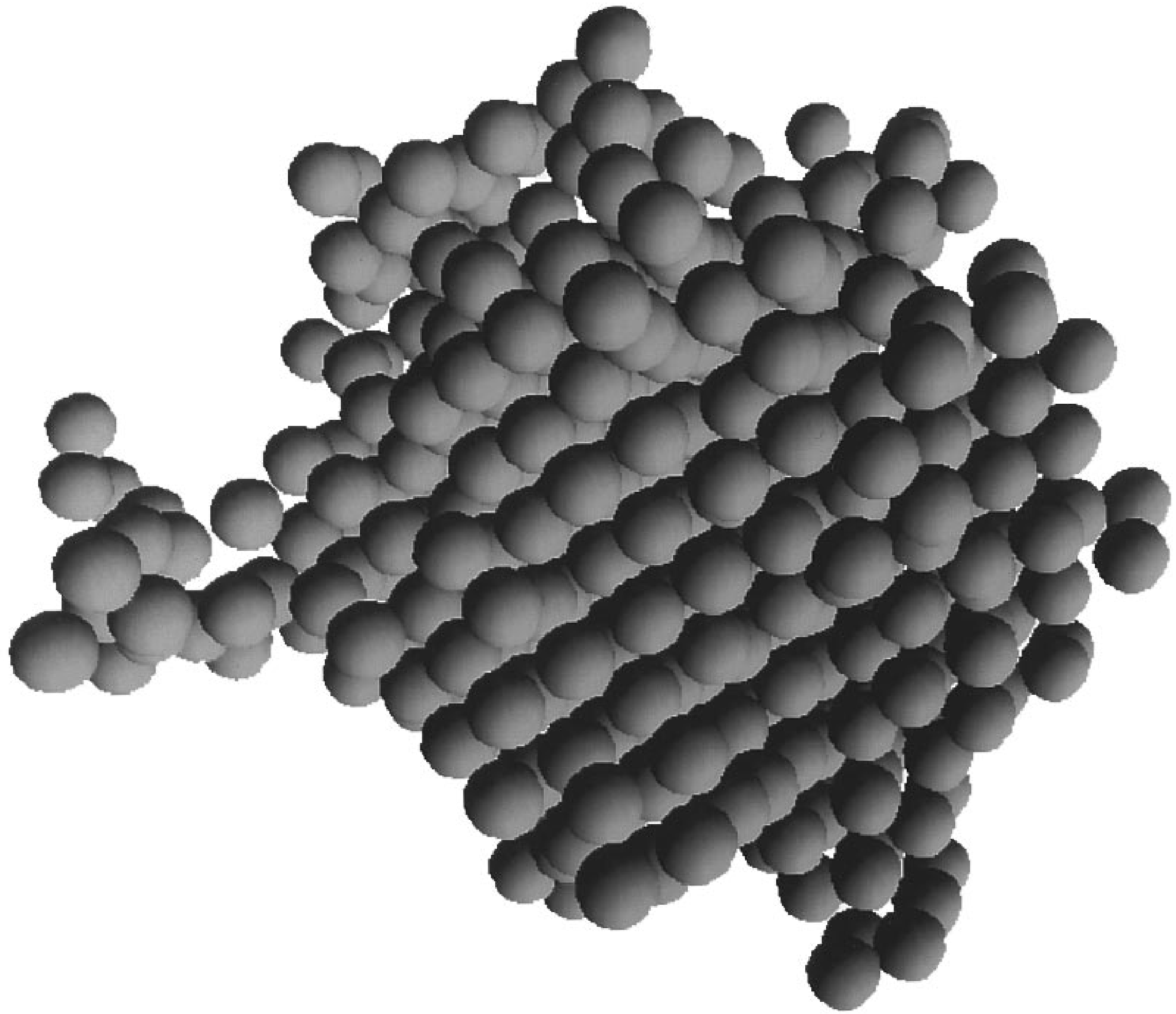
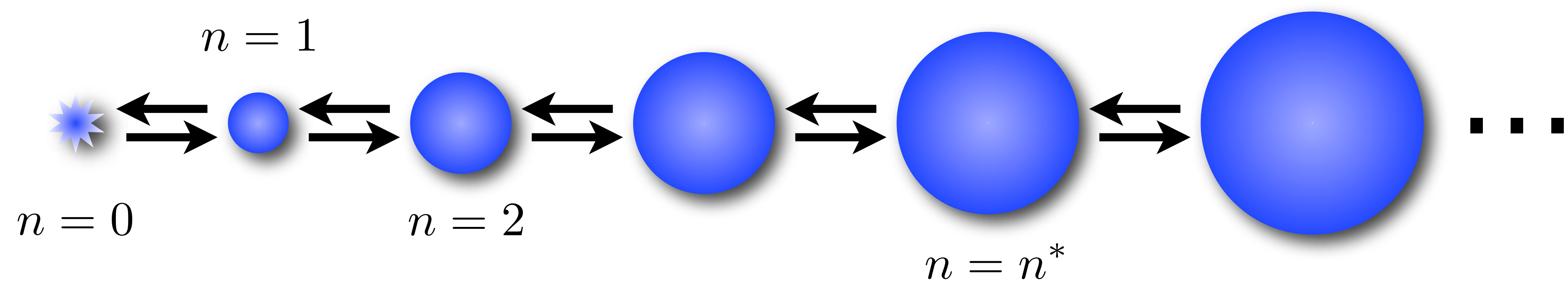


FIG. 5. Snapshot of the critical nucleus at 20% undercooling ($P=5.68$, $T=0.92$) in a Lennard-Jones system.

ten Wolde, et al., J. Chem. Phys., 1996

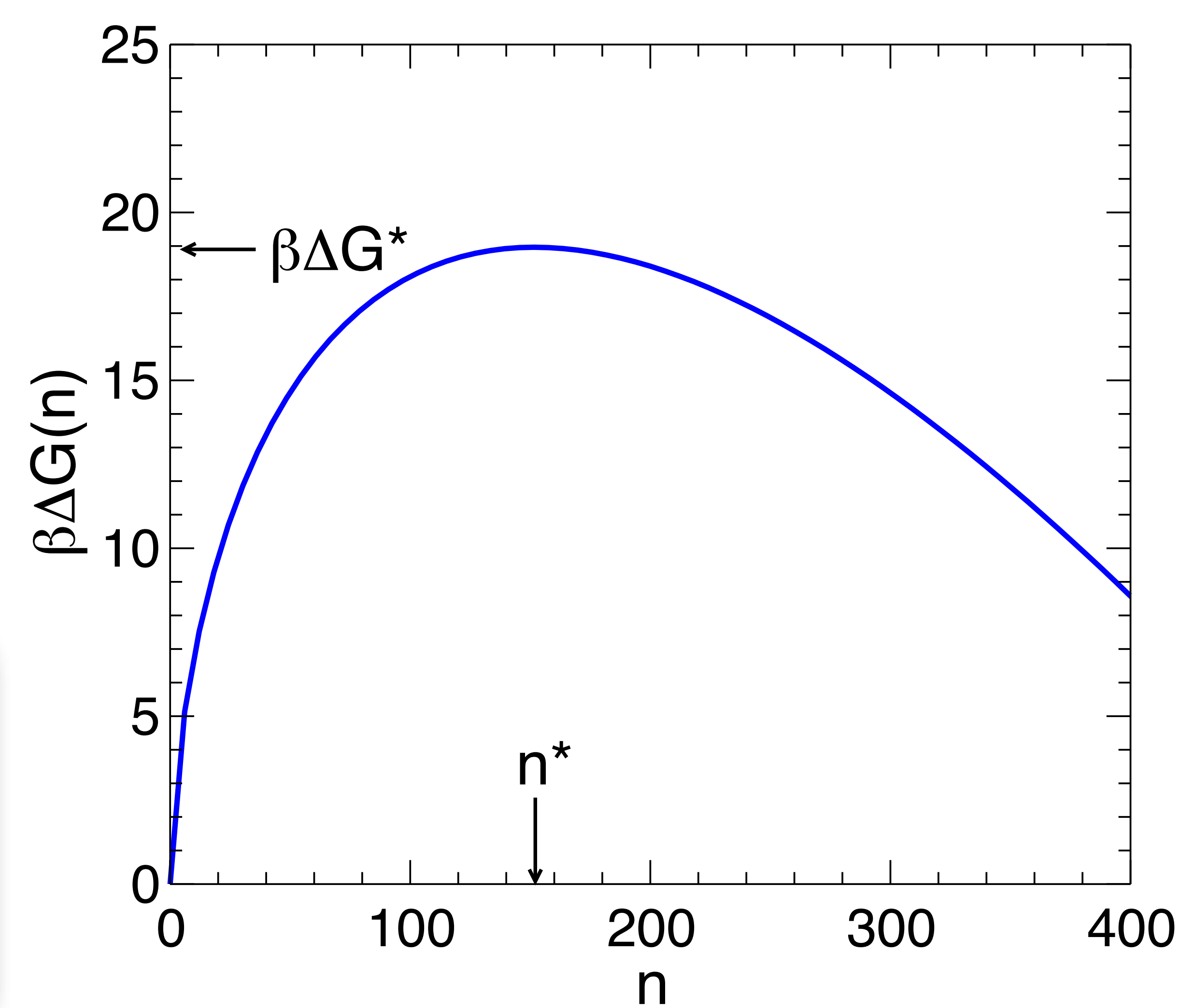
Classical nucleation theory (CNT)



Two challenges for finding $N(n)$ in simulations of crystal nucleation:

- Labelling particles as liquid-like or crystal-like. What's n?

- Sampling the equilibrium cluster distribution associated with a rare and irreversible process.

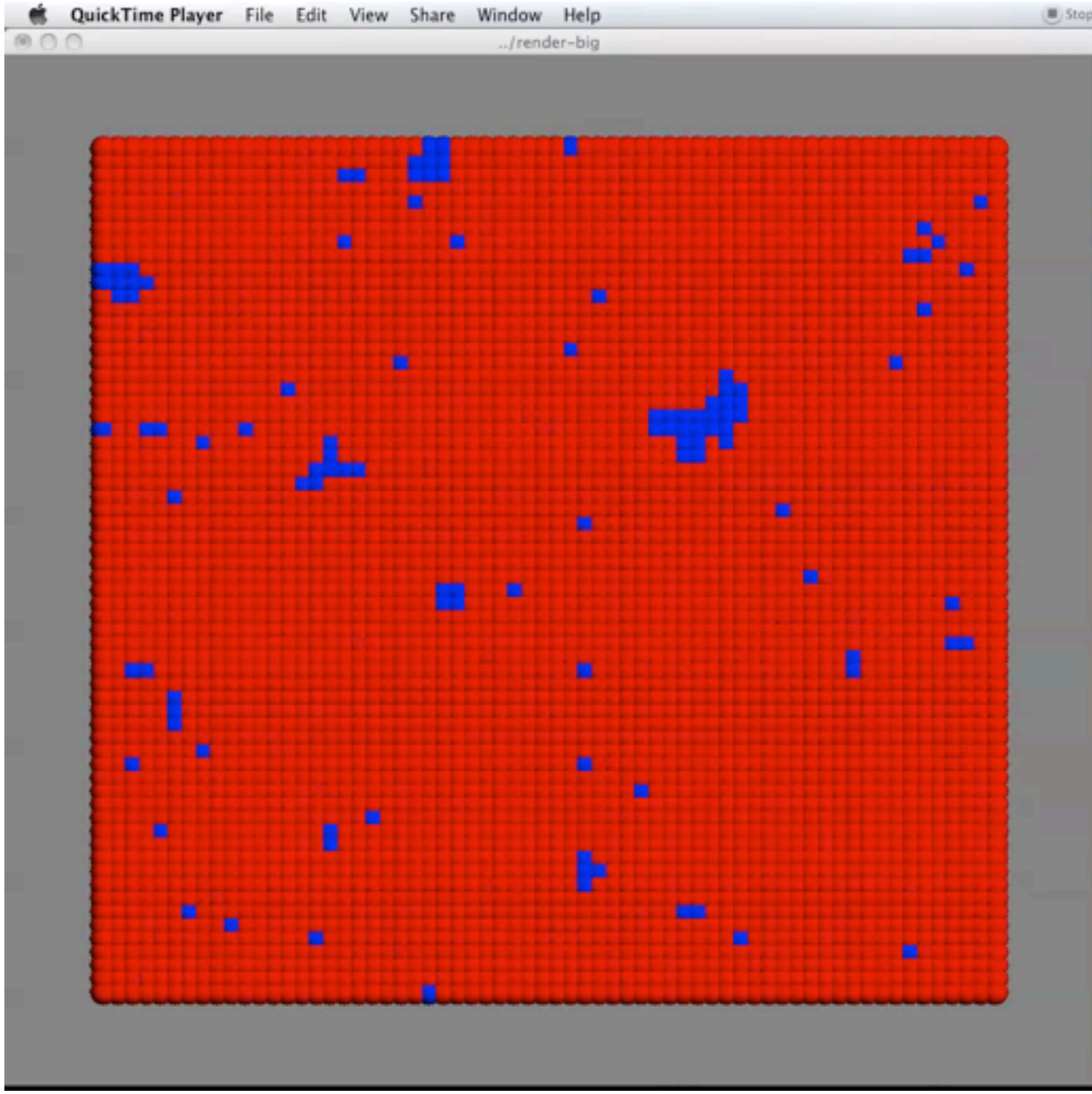


Case study: nucleation in the the 2D Ising model

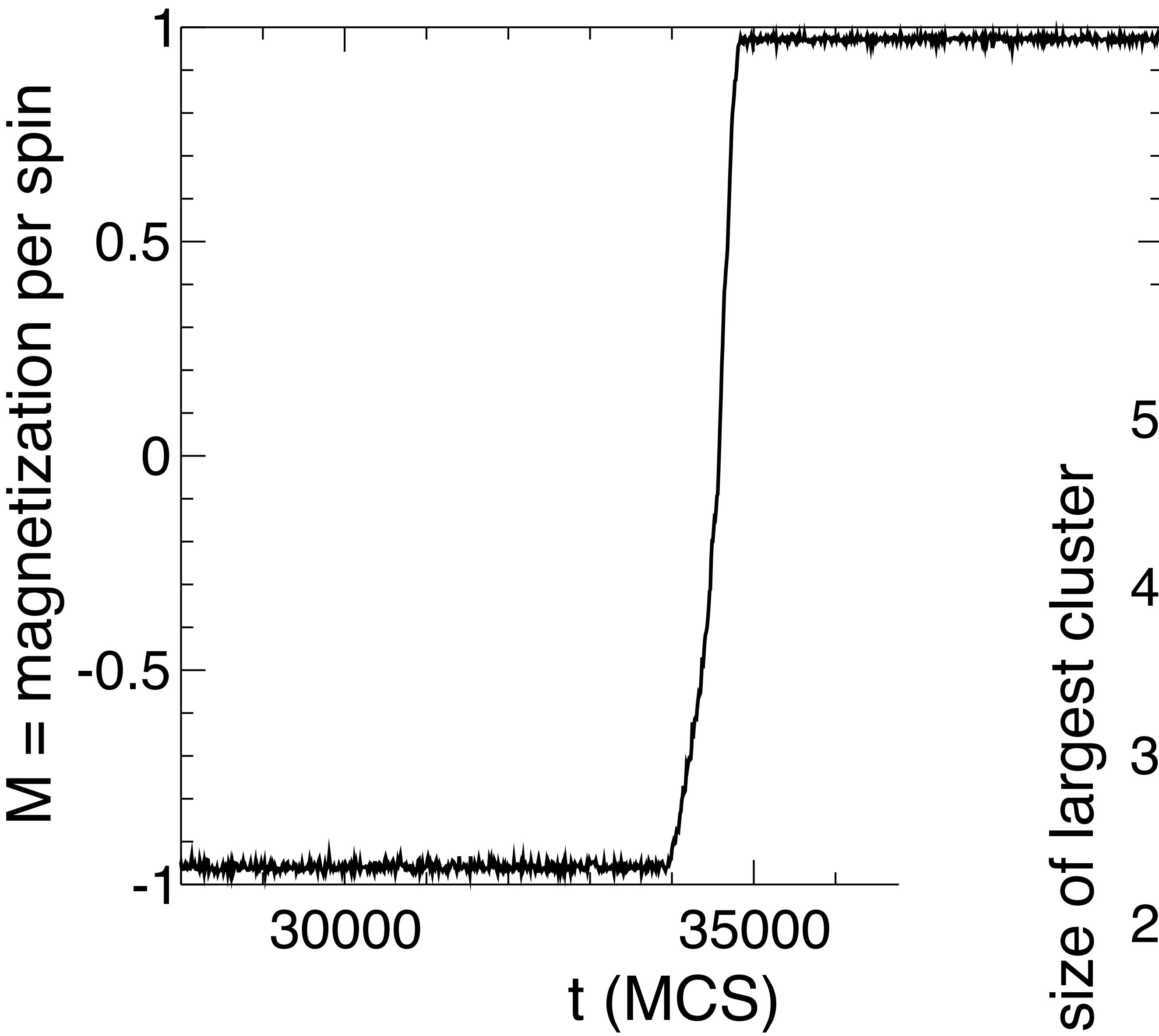
- 2D Ising model:

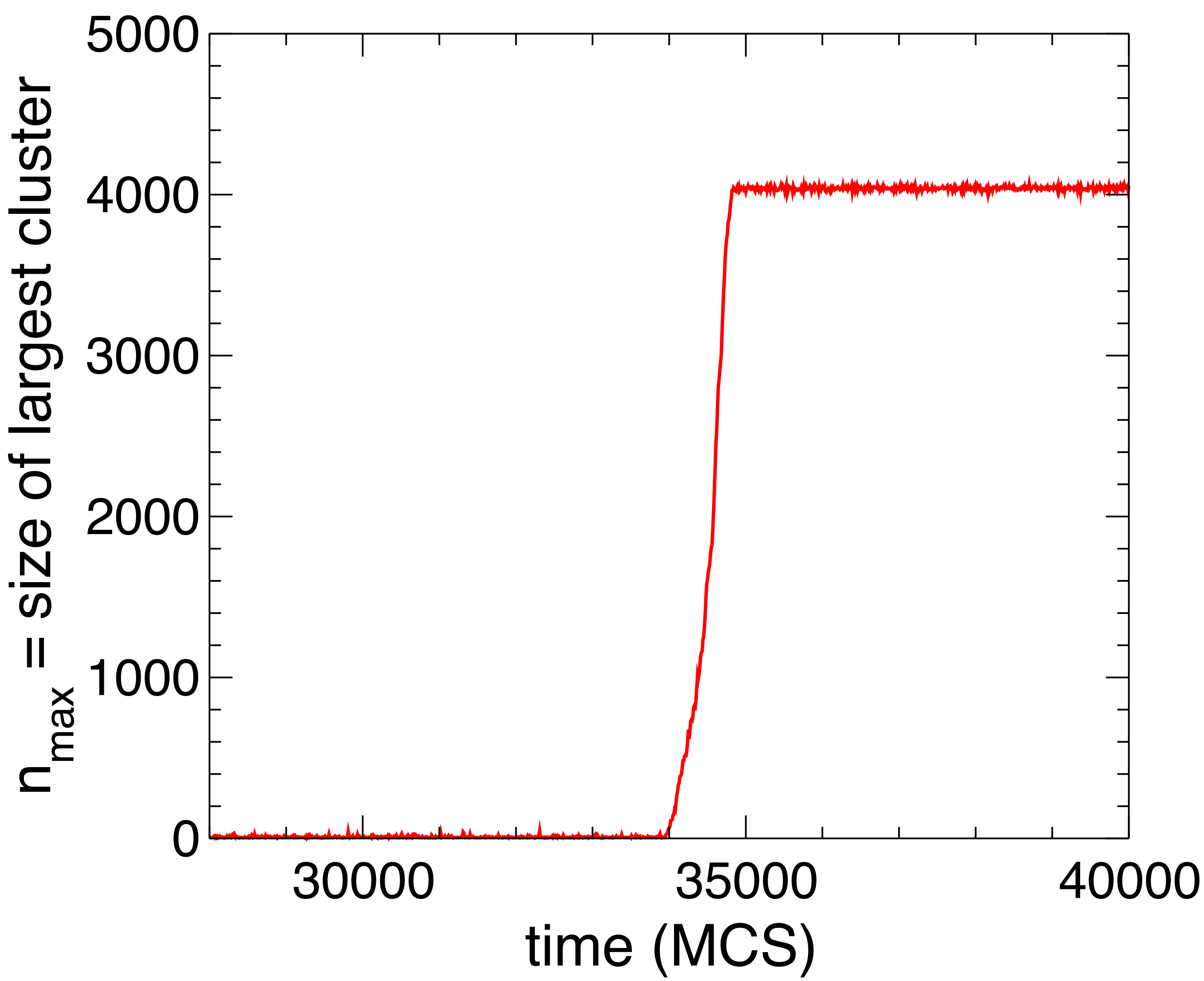
$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j + H \sum_i s_i$$

- Ferromagnetic: set $J = +1$
- $L = 64$
- $T = 1.72$, $T/T_c = 0.76$
- Initially all spins down, with $H = +0.2$
- red = down spins
- blue = up spins

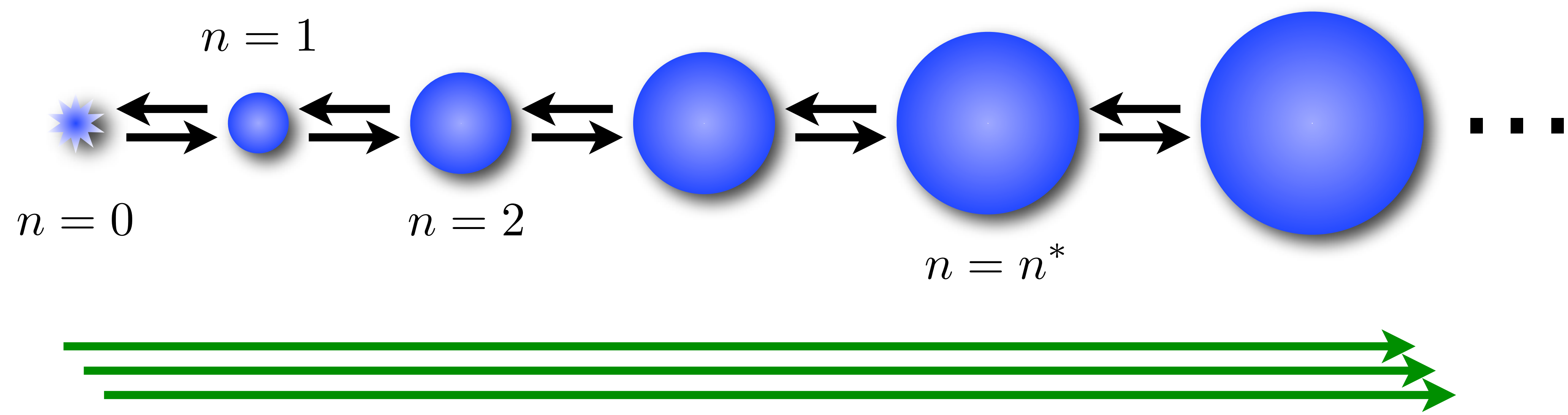


Order parameters: M and n_{max}

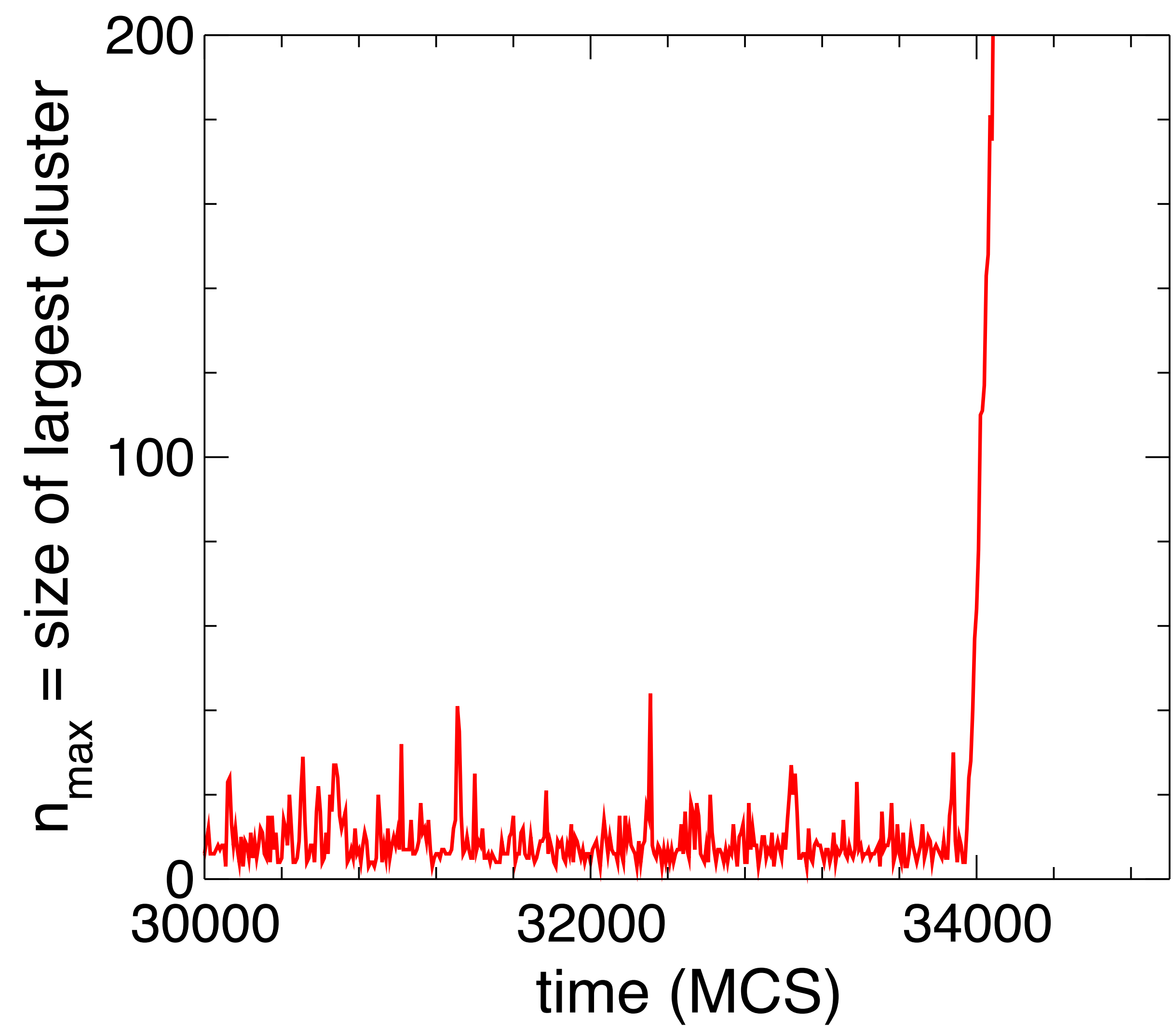




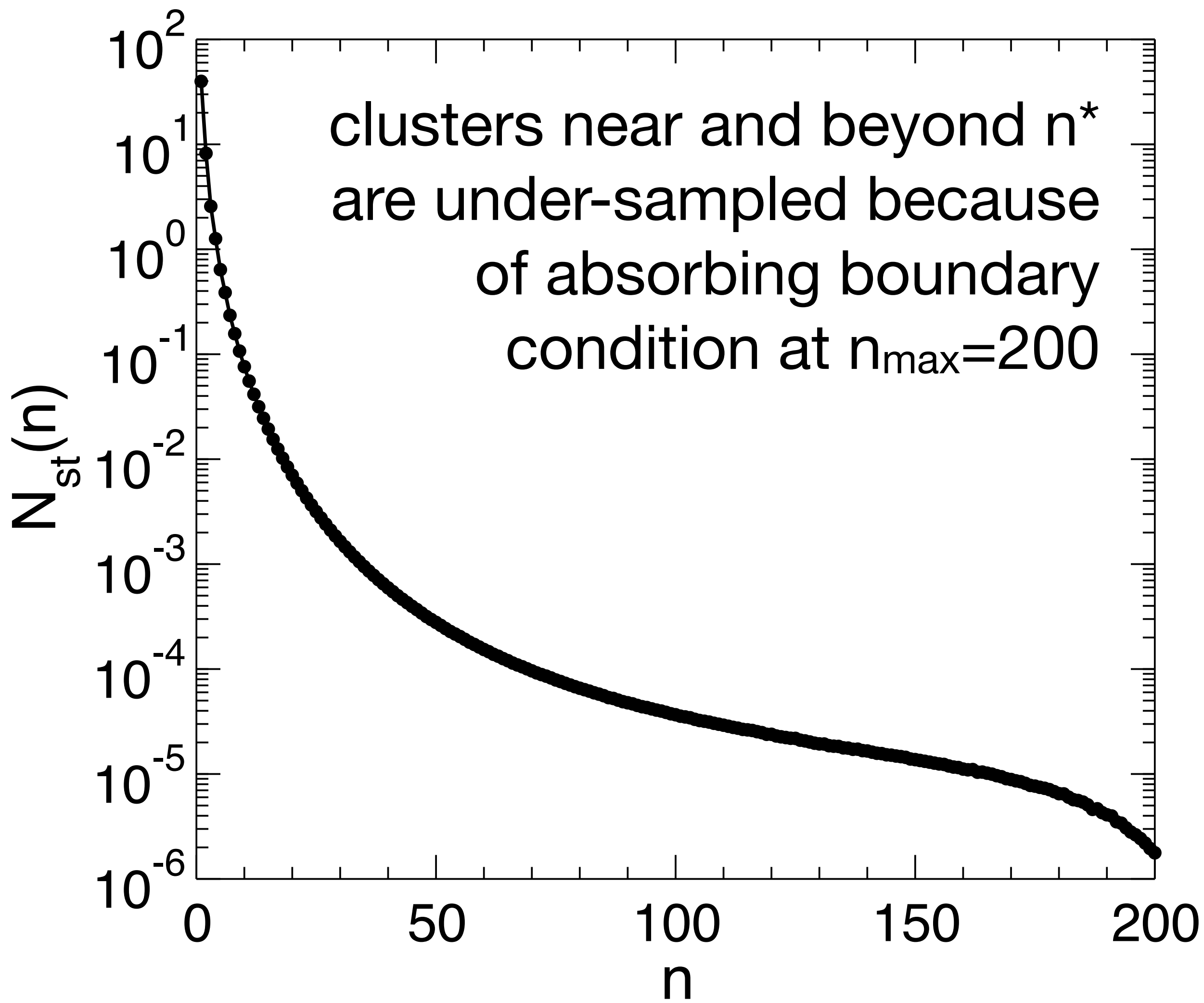
Finding N(n) in simulations of steady state nucleation

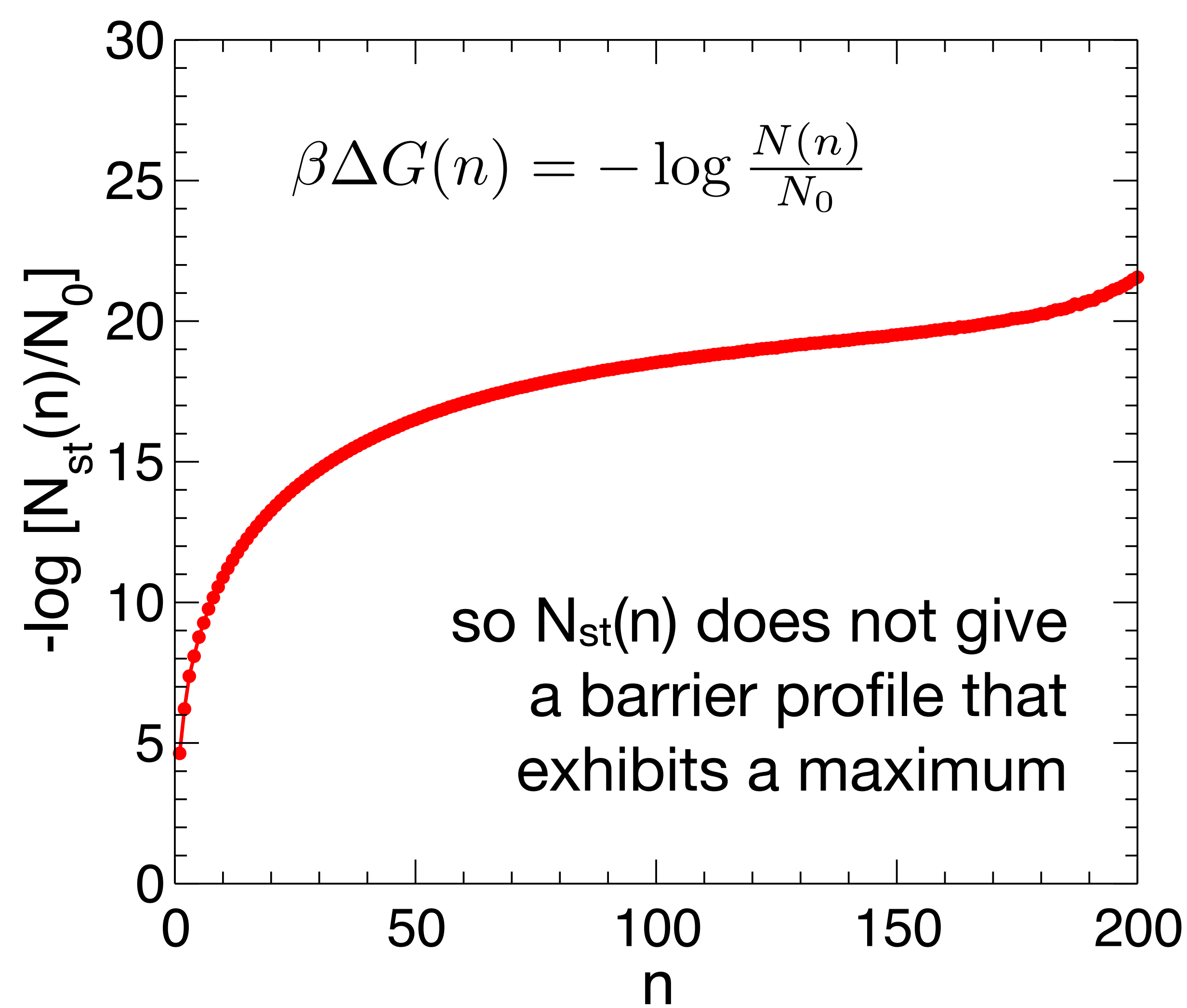


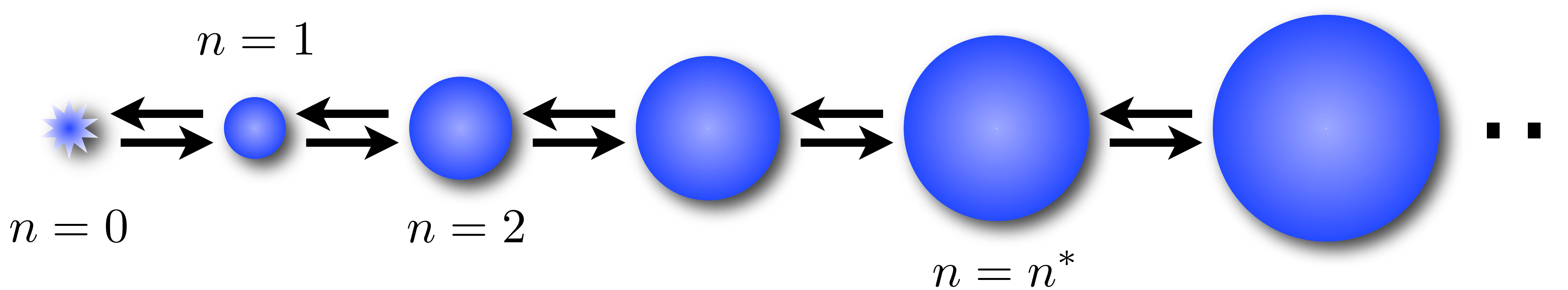
- Conduct many runs starting from all down spins.
- Under these conditions, the process is "steady state" nucleation in the sense that a well-defined metastable equilibrium is established prior to nucleation, and the rate at which nucleation occurs is independent of time.
- Absorbing boundary condition: runs are stopped when $n_{\max} = b = 200$.



Finding N(n) in simulations of steady state nucleation







Frenkel and Co.: Apply a constraint to find equilibrium N(n)

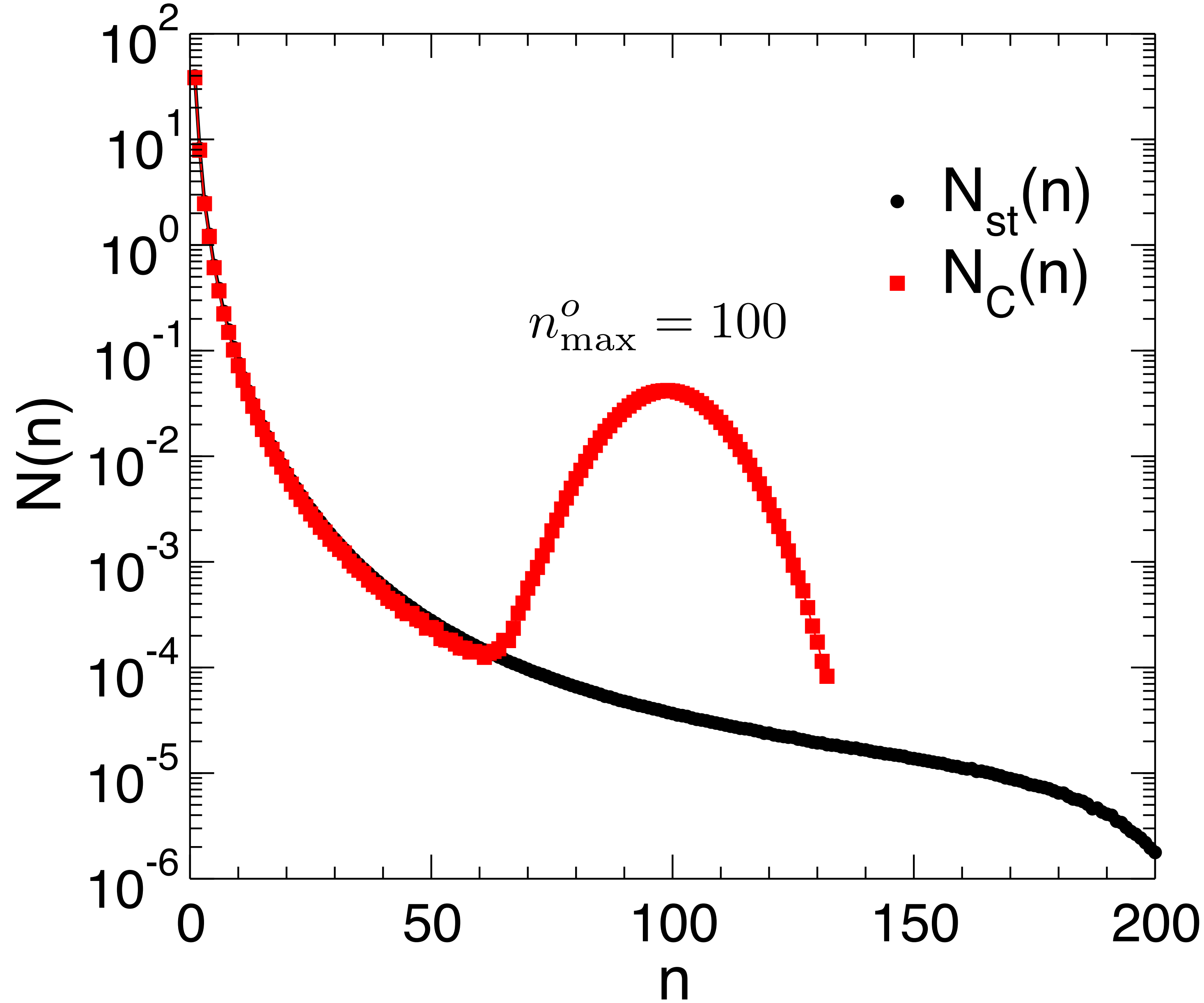
- Biased sampling applied to nucleation
- Constraint should be a property of the *system*. Let's choose $n_{\max}$.
- Apply constraint via the Hamiltonian:

$$\mathcal{H} = -J\sum_{\langle ij\rangle} s_i s_j + H\sum_i s_i + \phi(n_{\max}, n^o_{\max})$$

where,

$$\phi(n_{\max}, n^o_{\max}) = k(n_{\max} - n^o_{\max})^2$$

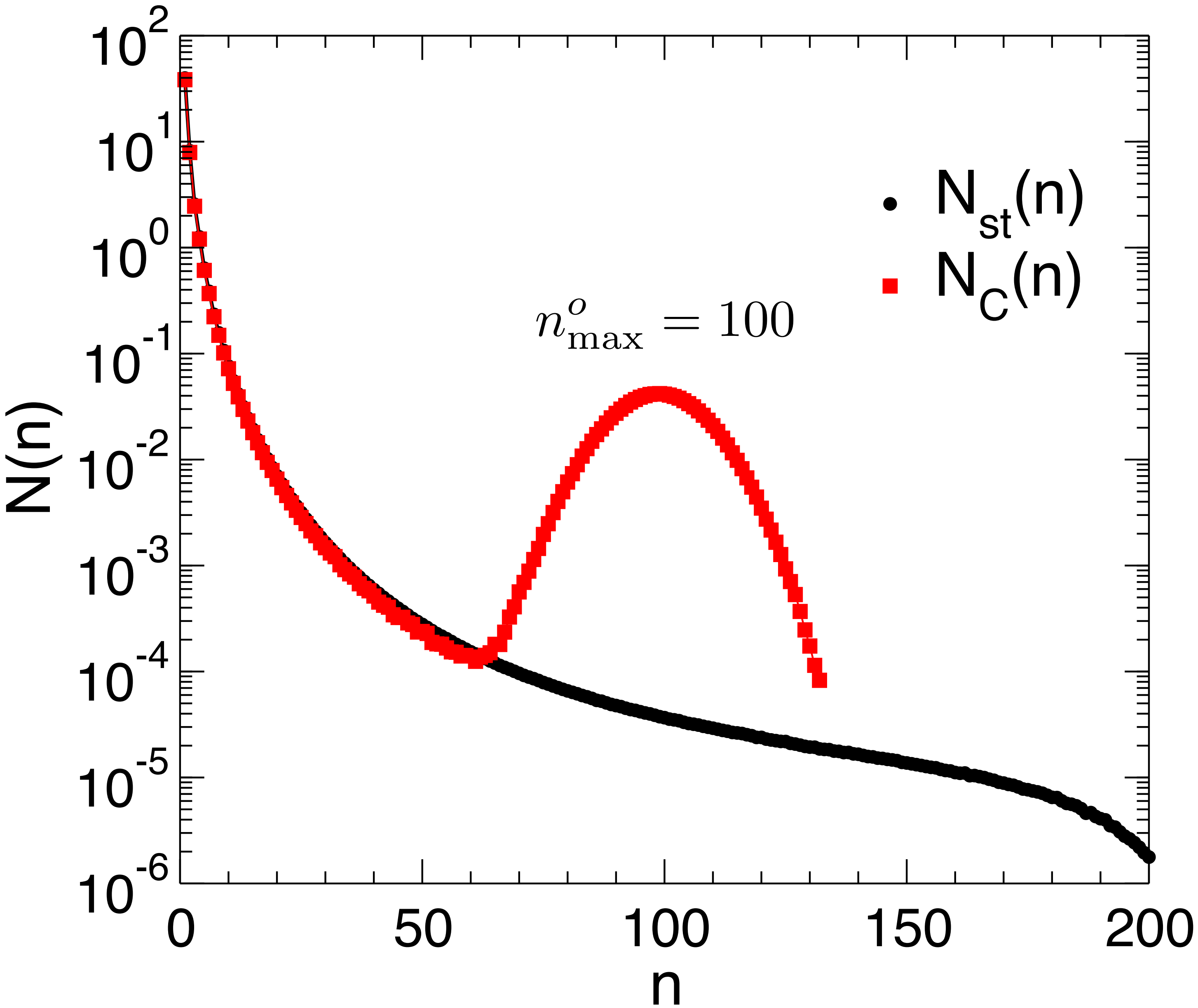
- $n^o_{\max}$ is a desired value of $n_{\max}$ around which we wish to sample.
- In simulation: Generate new states as before (MD or MC), but periodically accept/reject states with probability $\exp[-\beta\phi(n_{\max}, n^o_{\max})]$
- Gives $N_C(n)$, the cluster distribution in the constrained equilibrium.

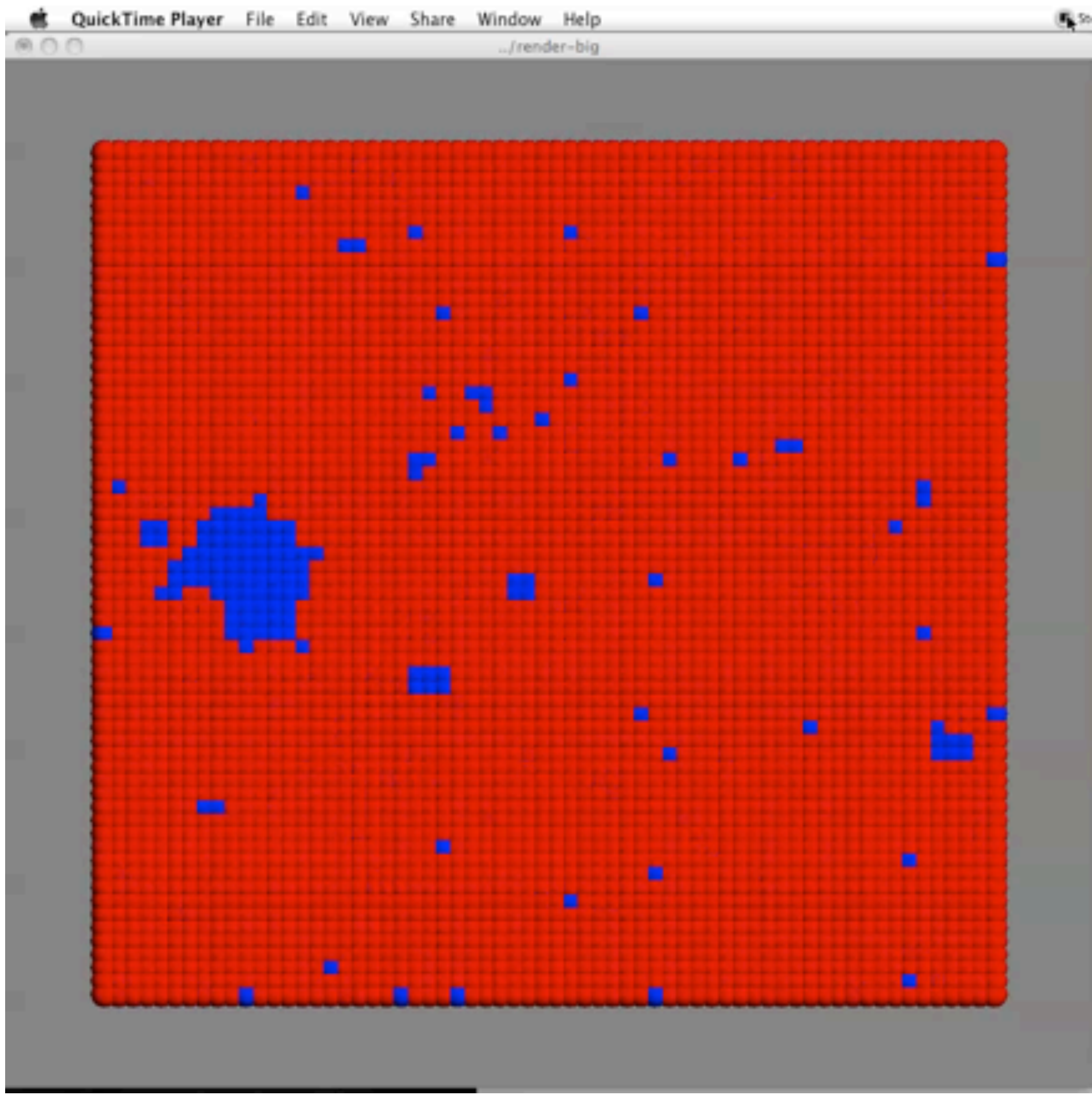


Review: Auer and Frenkel, Annual Reviews of Physical Chemistry, 2004

Based on "blue moon" ensemble first developed by Ciccotti and coworkers. See...
- E.A. Carter, et al., Chem. Phys. Lett, 156, 472 (1989).
- Sprik and Ciccotti, JCP, 109, 7737 (1998).

Apply a constraint to sample equilibrium N(n)





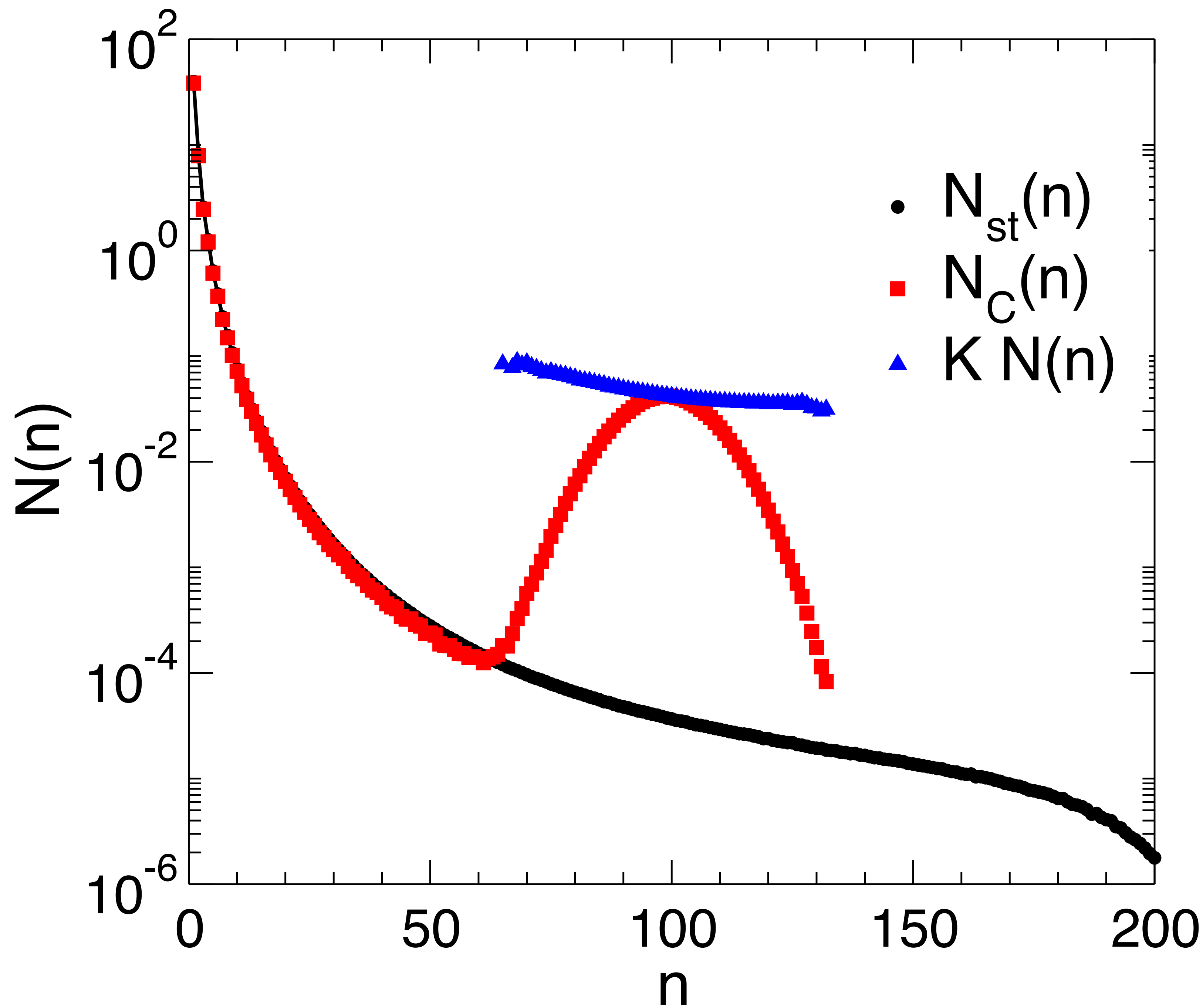
Guarantees that clusters sampled near $n=n^0_{max}$ are in equilibrium with both smaller and larger clusters.

Reweight constrained $N_C(n)$ to obtain equilibrium $N(n)$

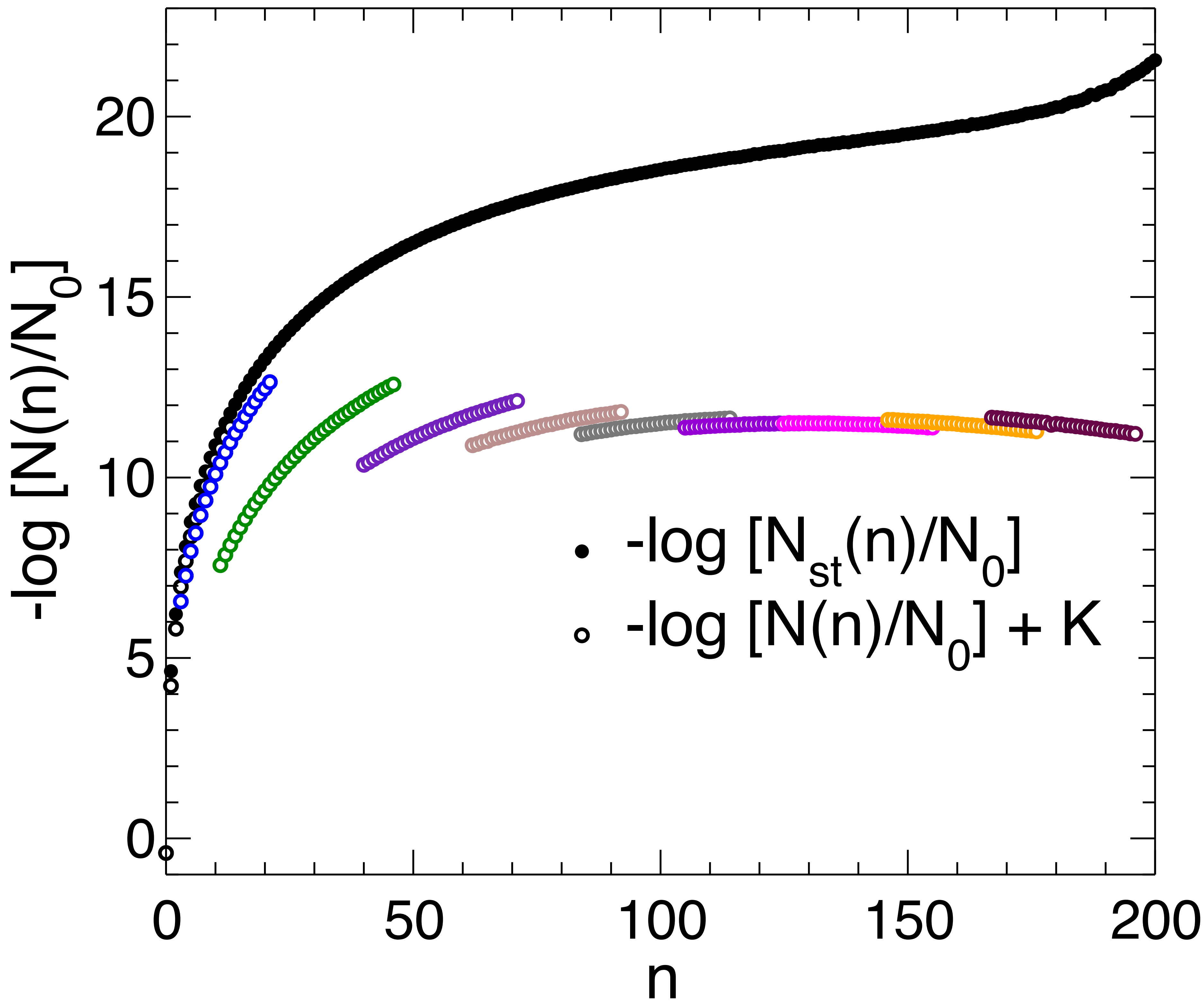
- Equilibrium $N(n)$ found from reweighted $N_C(n)$:

$$N(n) = K\langle N_C(n)\exp[\beta\phi(n_{\max}, n^o_{\max})]\rangle_C$$

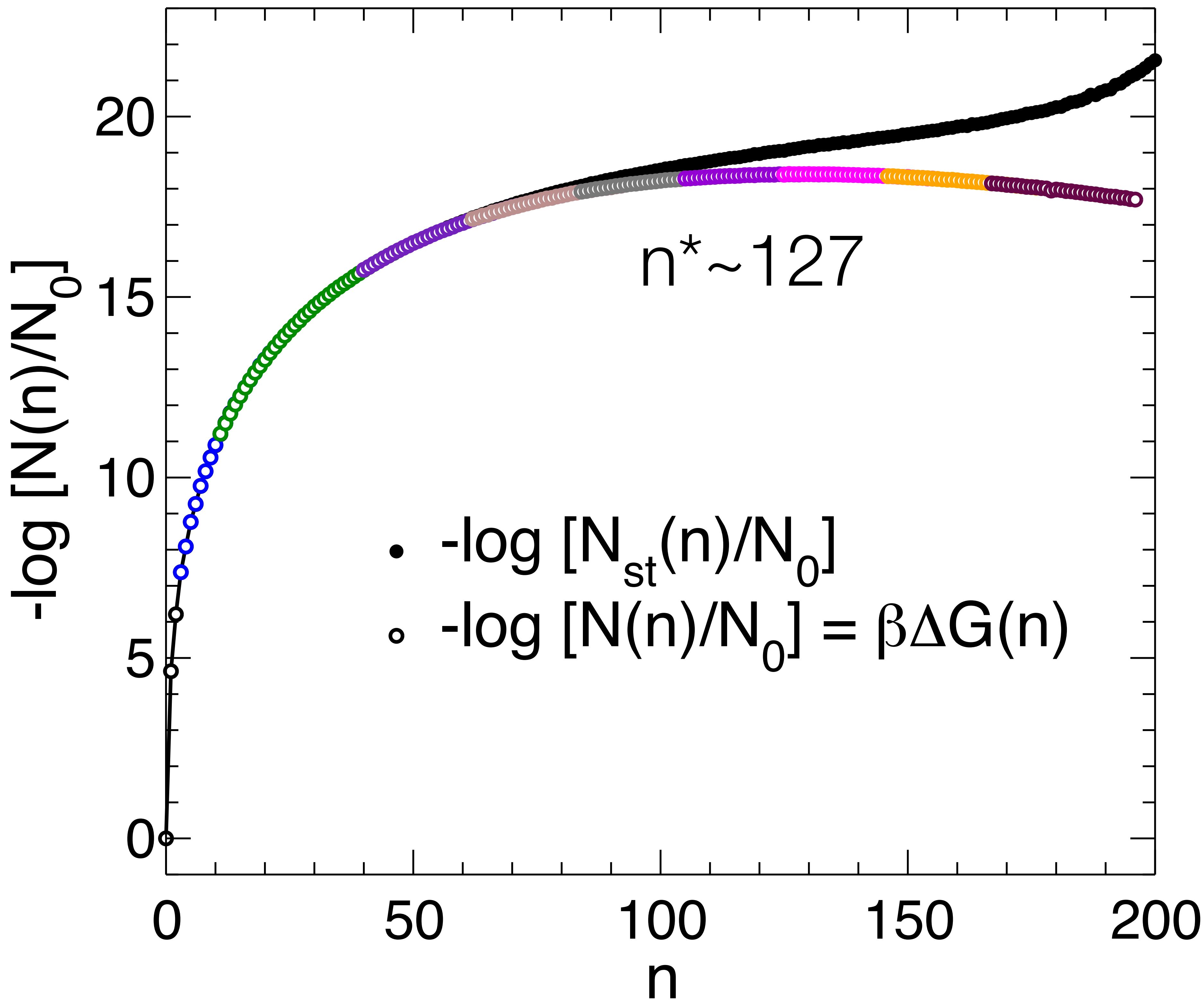
- $\langle\cdots\rangle_C$ is an average in the constrained ensemble.



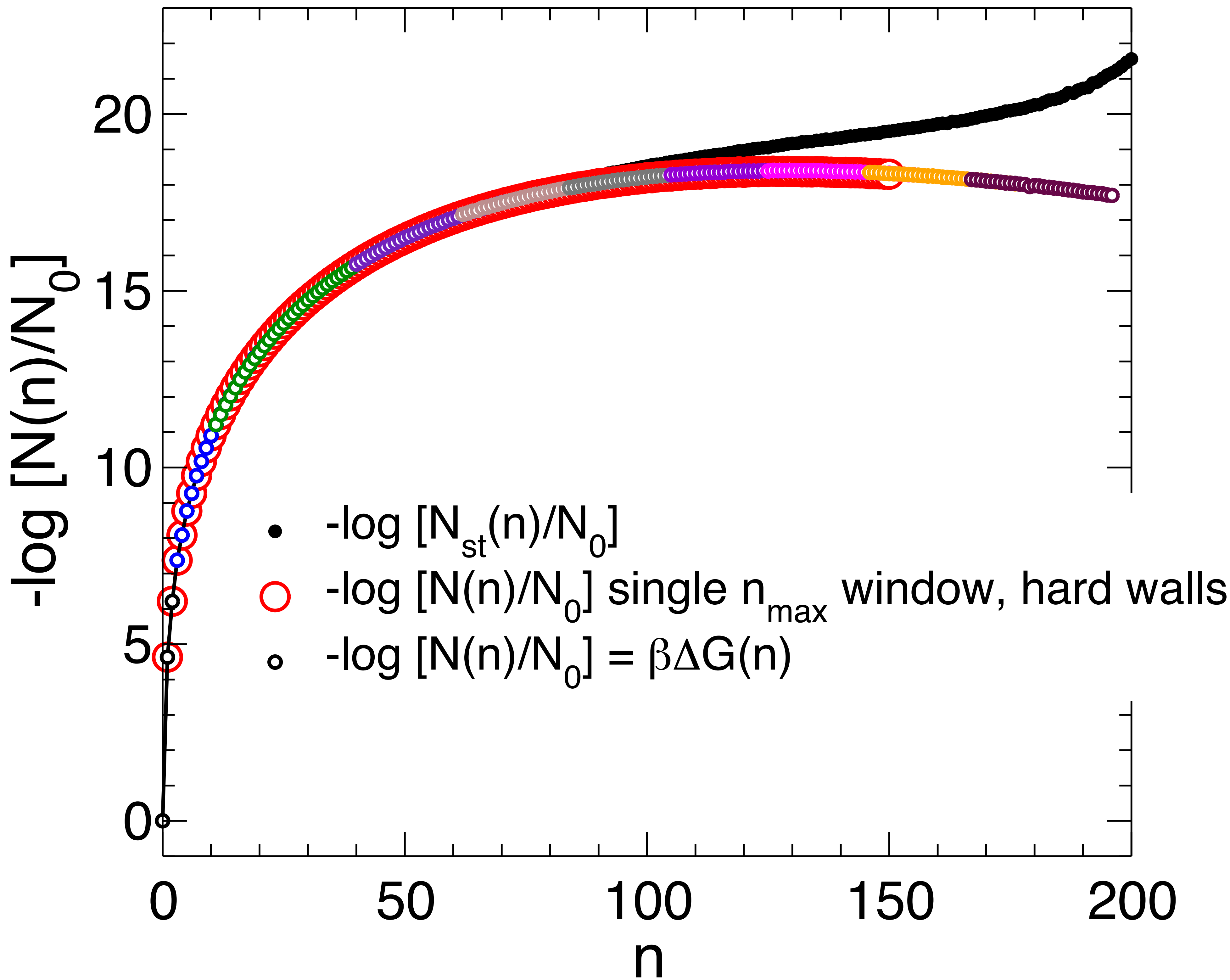
Find KN(n) for n near several values of n^0_{max}



Set $N(n)=N_0$ and splice $KN(n)$ curves together by shifting

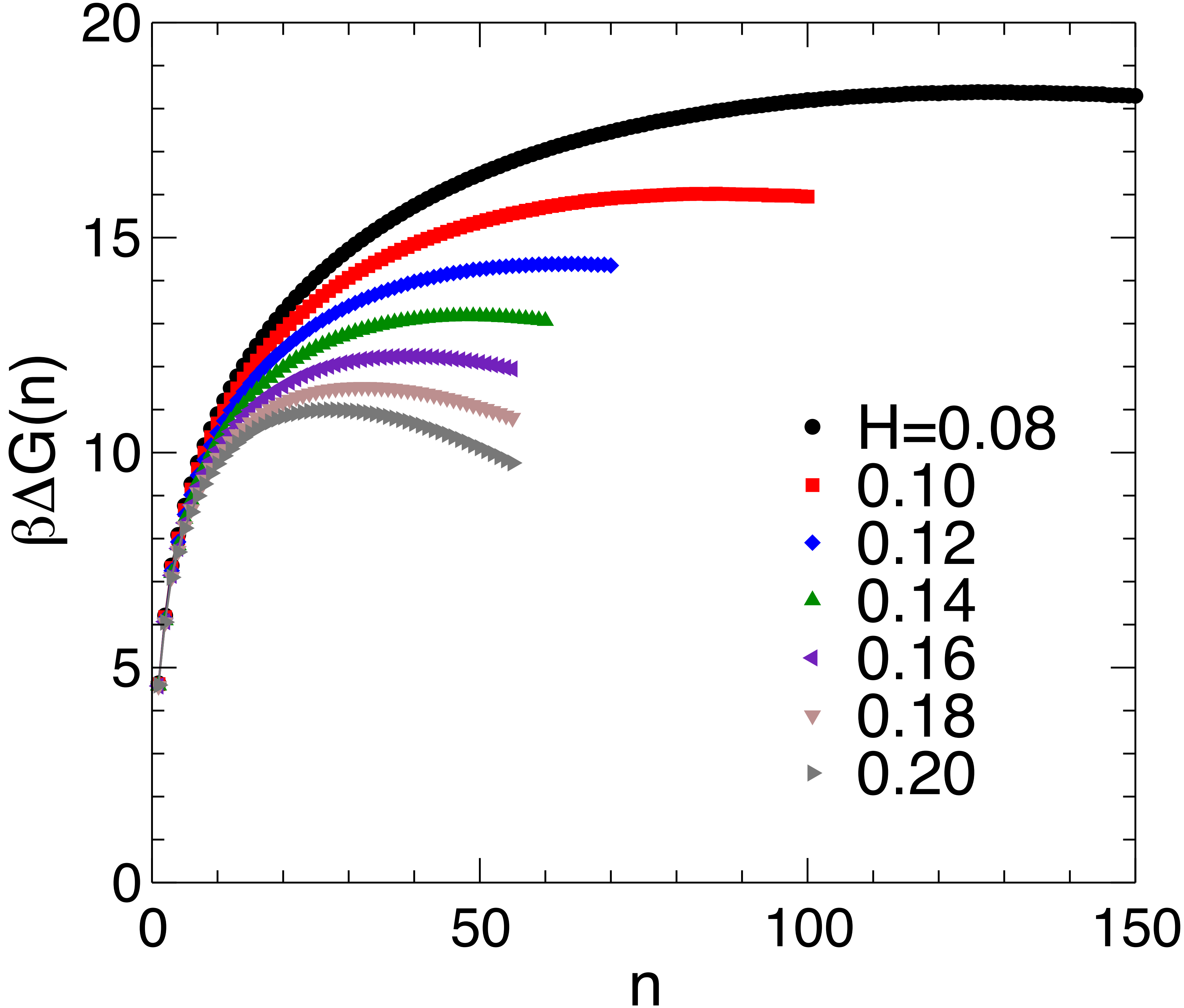


For low barriers, one sampling window may be enough



- System constrained by a reflecting boundary condition at n_{max}=150.
- No reweighting necessary: $N(n)=N_C(n)$

Barrier profiles as a function of H field

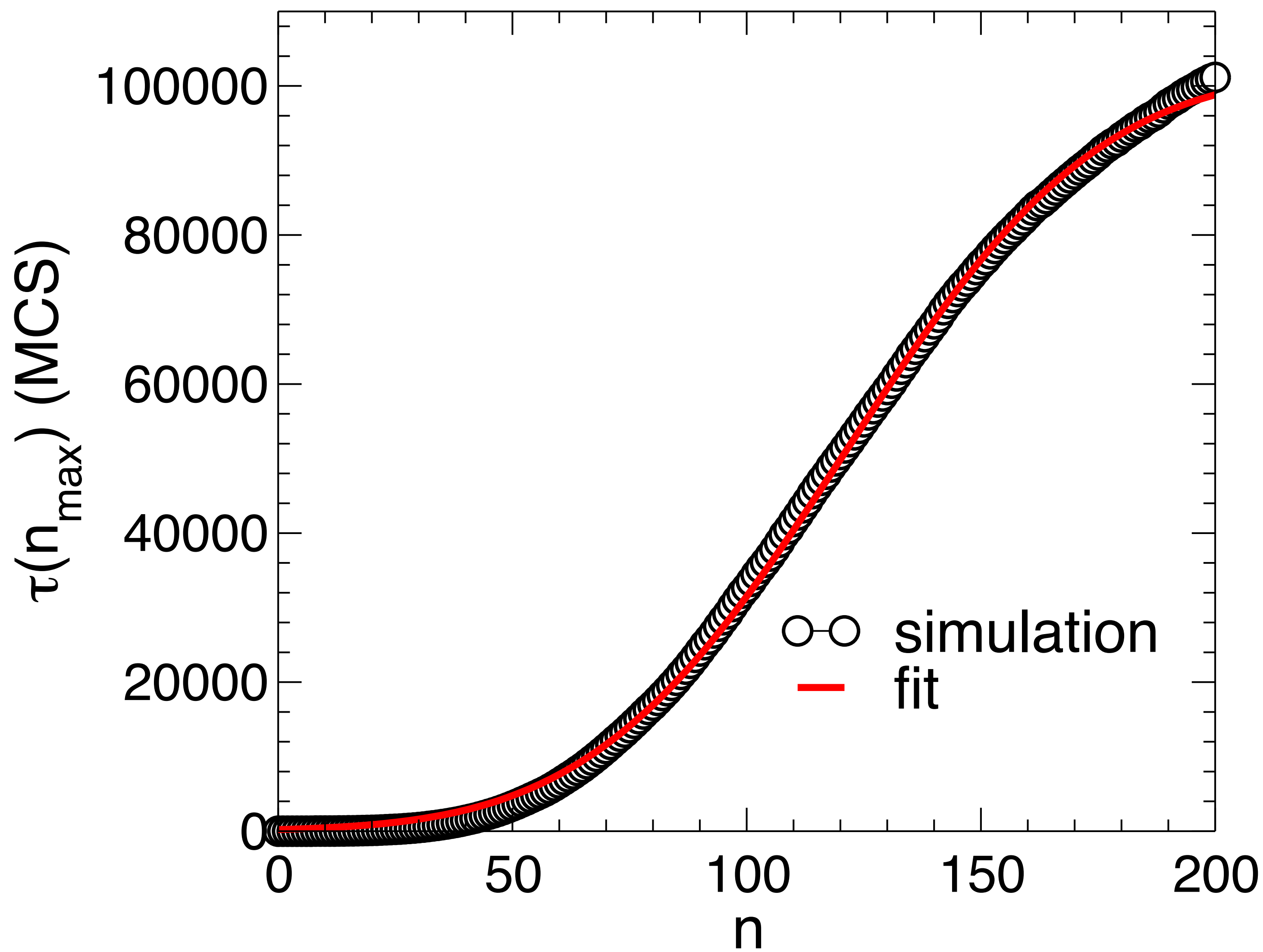


Reguera and Co.: "Mean first passage time" approach

- Uses data from unconstrained, steady-state nucleation runs
- Allows evaluation of barrier profiles as well as kinetic info from a single set of runs.
- $\tau(n_{\max})$ is the average time at which the largest cluster in the system first reaches a size $n_{\max}$.
- Predicts for $\tau(n_{\max})$:

$$\tau(n_{\max}) = \frac{1 + \mathrm{erf}[c(n_{\max} - n^*)]}{2JV}$$

- Here, fit gives $n^* = 121$. Umbrella sampling gave $n^* = 127$.



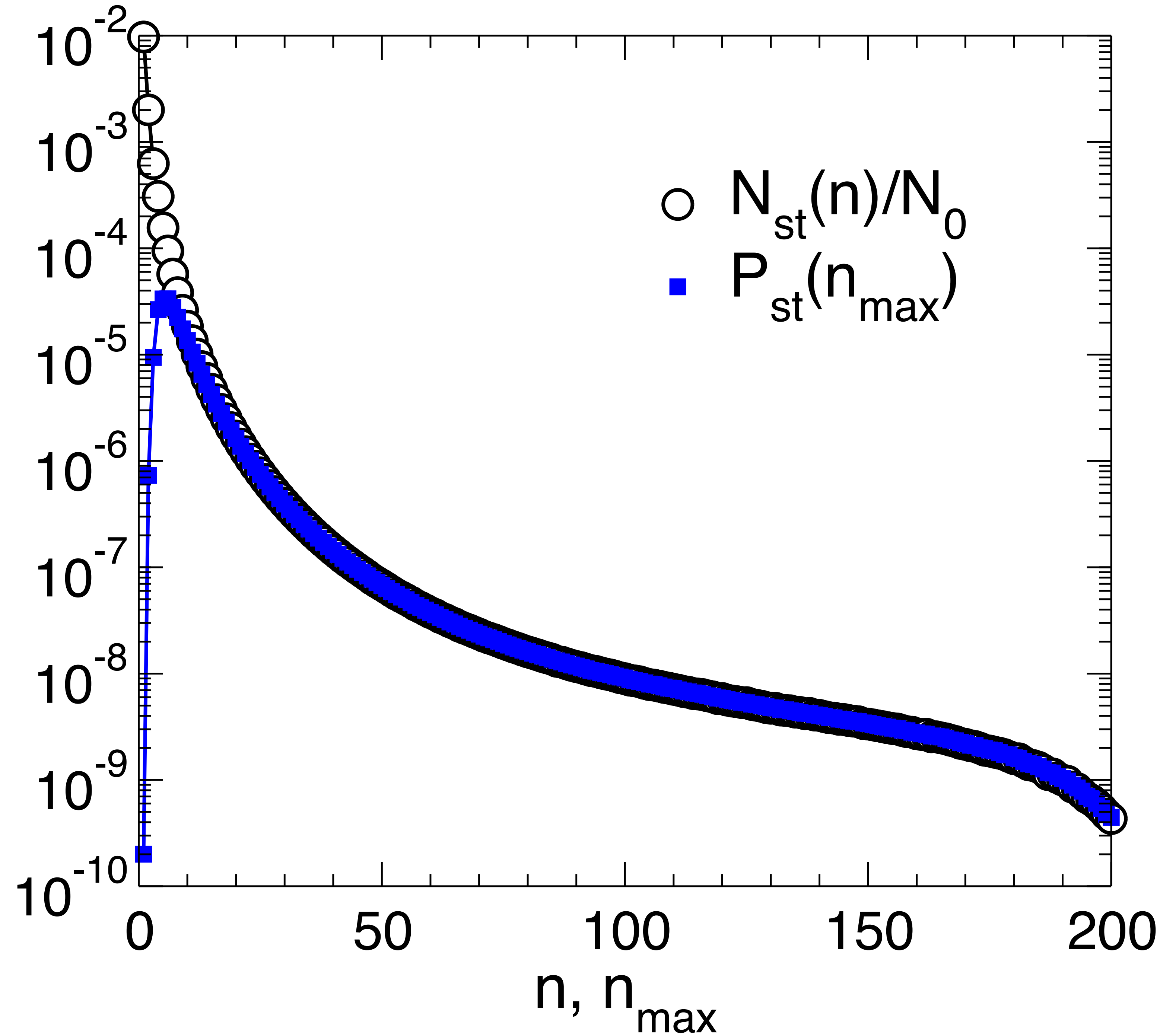
J. Wedekind, R. Strey, and D. Reguera, J. Chem. Phys. 126, 134103, 2007.
J. Wedekind and D. Reguera, J. Phys. Chem. B 112, 11060, 2008.

Reguera and Co.: "Mean first passage time" approach

- Also need $P_{\rm st}(n_{\rm max})$, the steady-state probability that the largest cluster in the system is of size $n_{\rm max}$.
- When clusters of size $n_{\rm max}$ are rare,

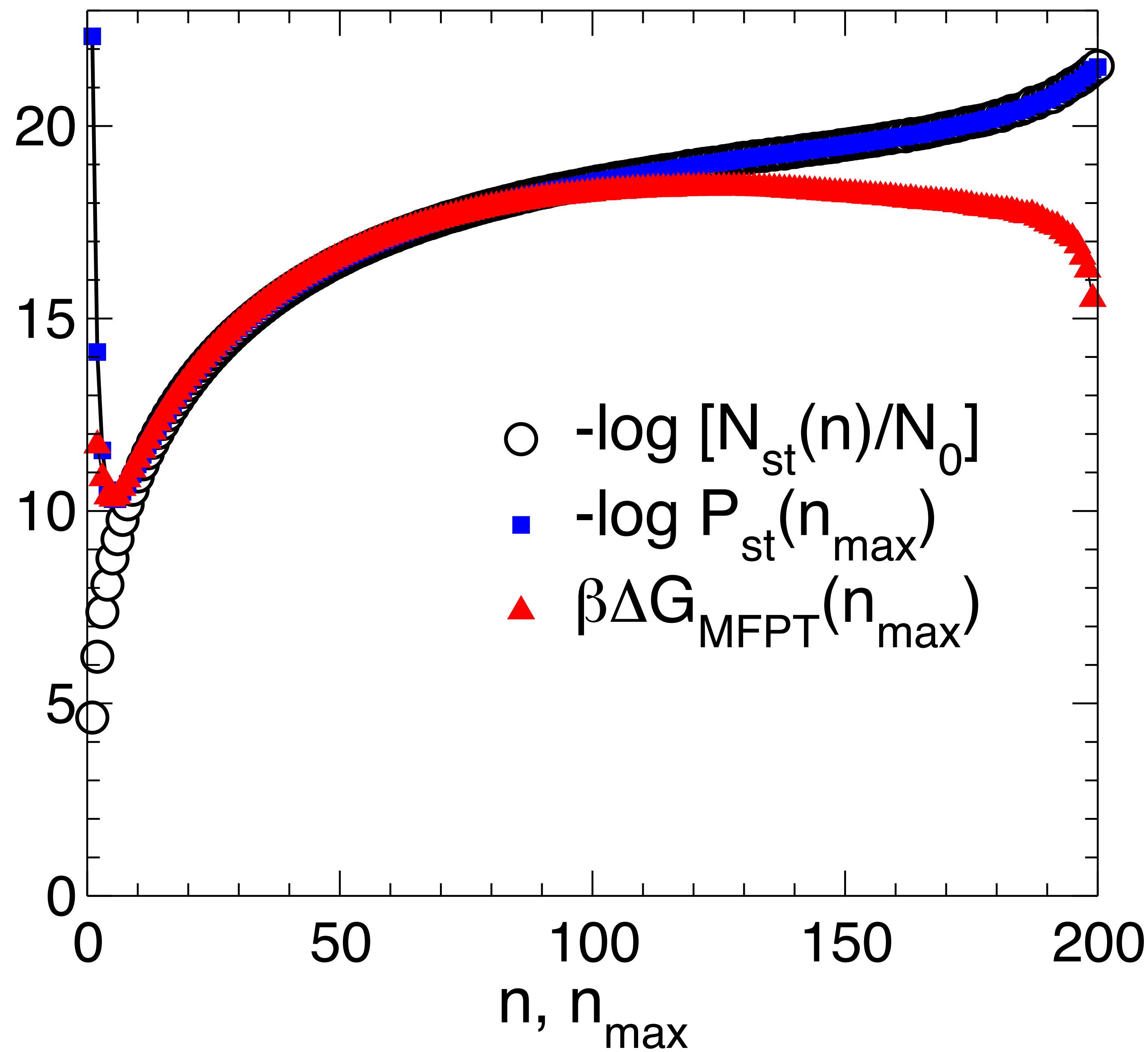
$$P_{\rm st}(n_{\rm max}) = N_{\rm st}(n)/N_0$$

- Note the maximum in $P_{\rm st}(n_{\rm max})$ at small $n_{\rm max}$. It's unlikely that the largest cluster is extremely small.



Reguera and Co.: “Mean first passage time” approach

- Method corrects $P_{\rm st}(n_{\max})$ using $\tau(n_{\max})$ to give $\beta\Delta G_{\rm MFPT}(n_{\max})$

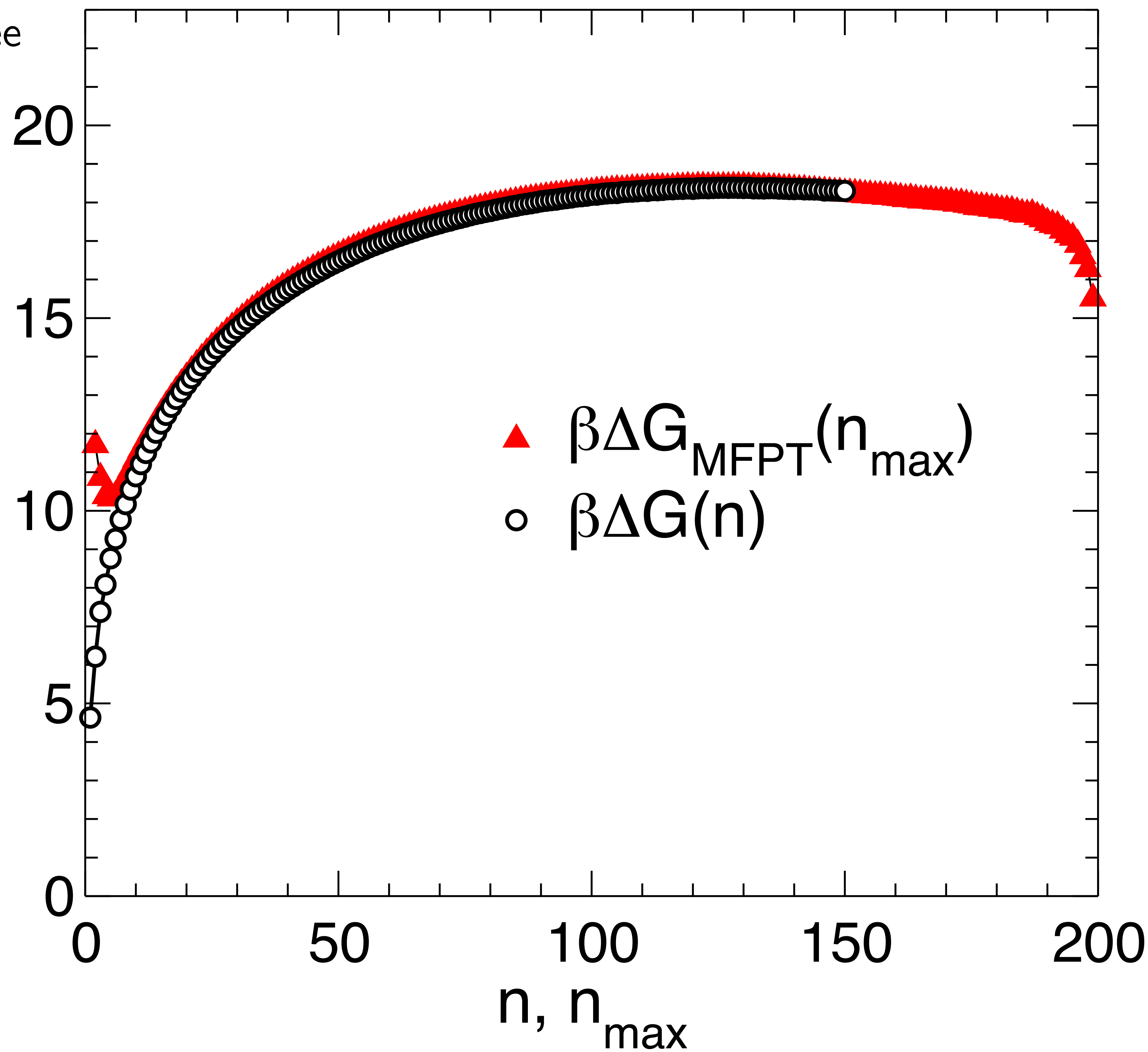


$$B(x) = -\frac{1}{P_{\rm st}(x)}\left[\int_x^b P_{\rm st}(x')\,{\rm d}x' - \frac{\tau(b)-\tau(x)}{\tau(b)}\right]$$

$$\beta\Delta G(x) = \ln(B(x)) - \int \frac{{\rm d}x'}{B(x')} + C$$

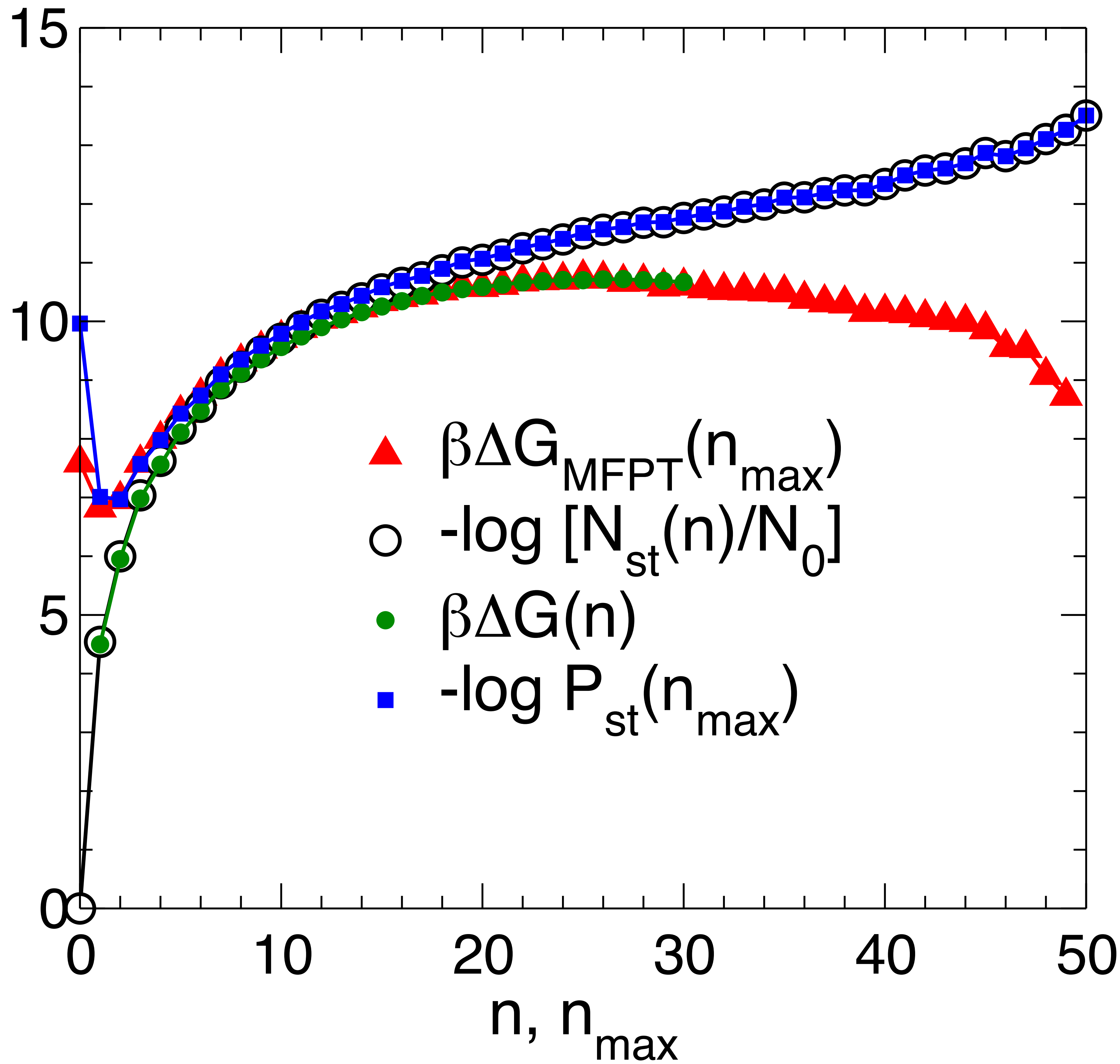
Comparison of MFPT and biased sampling

- MFPT and biased sampling agree at large n.
- Caution: When barriers become low ($< 10kT$), the assumption that larger clusters are rare begins to break down. See...
- P. Bhimalapuram, S. Chakrabarty, and B. Bagchi, Phys. Rev. Lett. 98, 206104, 2007.
- L. Maibaum, Phys. Rev. Lett. 101, 256102, 2008.
- J. Wedekind, et al., J. Chem. Phys. 11, 114506, 2009.



<u>Homework!</u> Do L=16 Ising model on your laptops (~30 cpu min)

L=16,
H=0.2,
T=1.72



THE JOURNAL OF CHEMICAL PHYSICS **131**, 104503 (2009)

Test of classical nucleation theory and mean first-passage time formalism on crystallization in the Lennard-Jones liquid

Sarah E. M. Lundrigan and Ivan Saika-Voivod[a)]
Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John's, Newfoundland and Labrador A1B 3X7, Canada

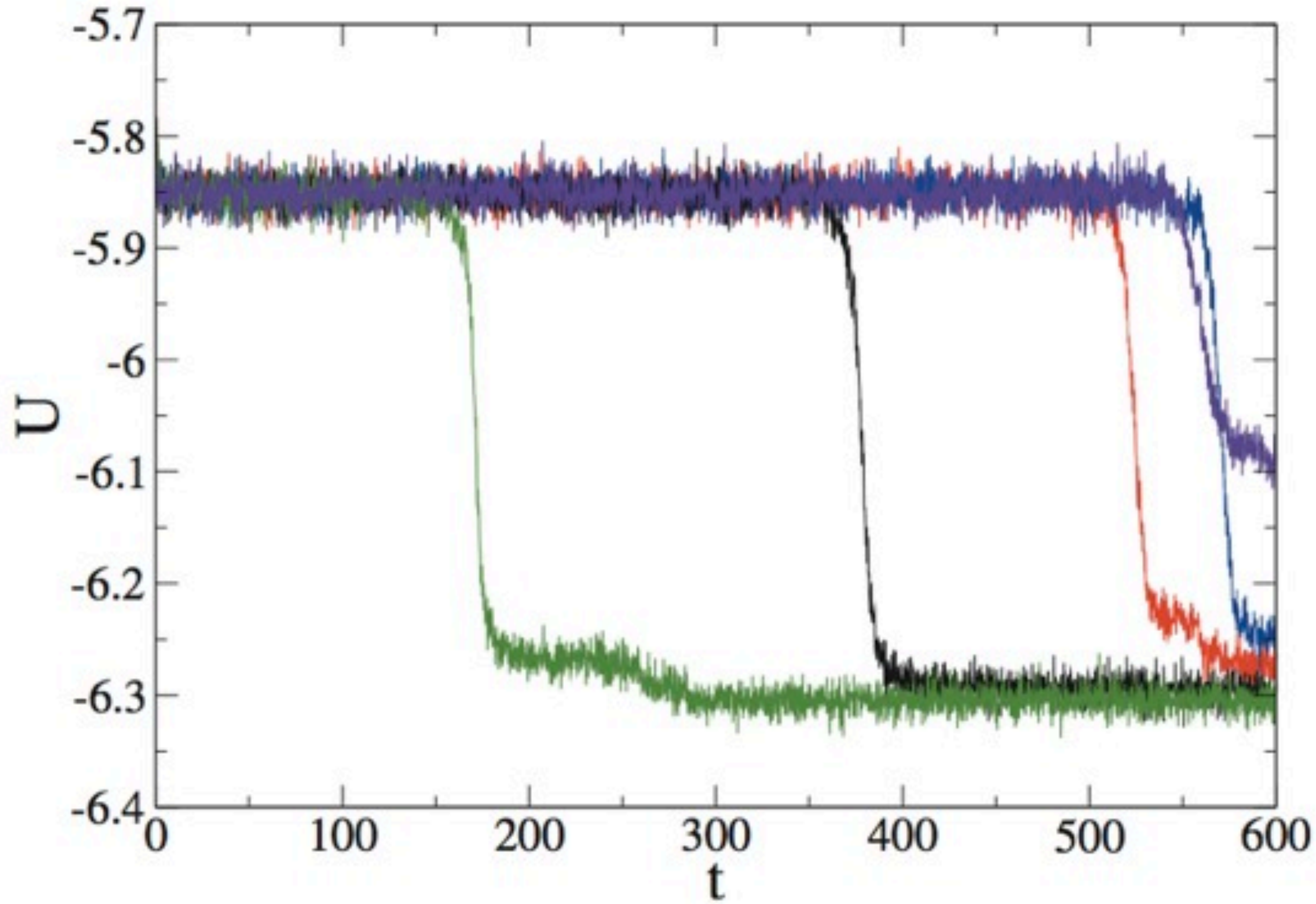
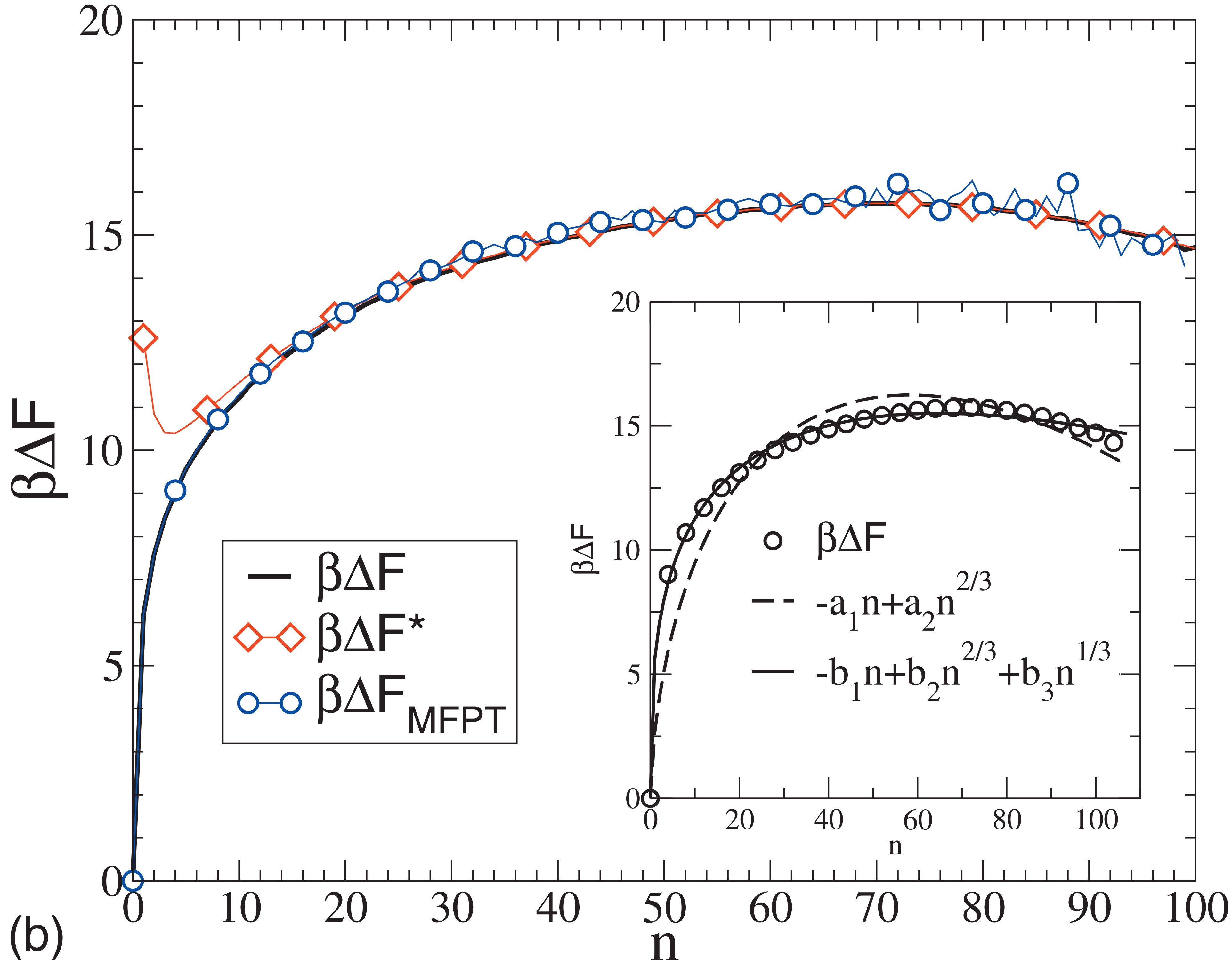


FIG. 1. A sampling of potential energy time series for crystallizing MD runs. Equilibrium configurations drawn from $T=1.2$ are quenched to $T=0.58$ at $t=0$ by changing the Nosé–Hoover thermostat setting. For the data shown here, it is clear that a metastable liquid state is attained prior to nucleation.

Comparison of MFPT and biased sampling approaches in LJ crystal nucleation



Lundrigan and Saika-Voivod, JCP, 2009

What about kinetics?

- In CNT, the nucleation rate is

$$J = K \exp(-\beta \Delta G^*)$$

- $K = \rho_n Z f_c^+$
- ρ_n is the number density of the particles.
- Z is the Zeldovich factor:

$$Z = \sqrt{\frac{\beta|\Delta\mu|}{6\pi n^*}} = \sqrt{\frac{\beta|G''(n^*)|}{2\pi}}$$

- f_c^+ is the attachment rate of particles to the critical nucleus, given by,

$$f_c^+ = \frac{24D(n^*)^{2/3}}{\lambda^2} = \frac{\langle [n^*(t) - n^*(0)]^2 \rangle}{2t}$$

Lundrigan and Saika-Voivod, JCP, 2009

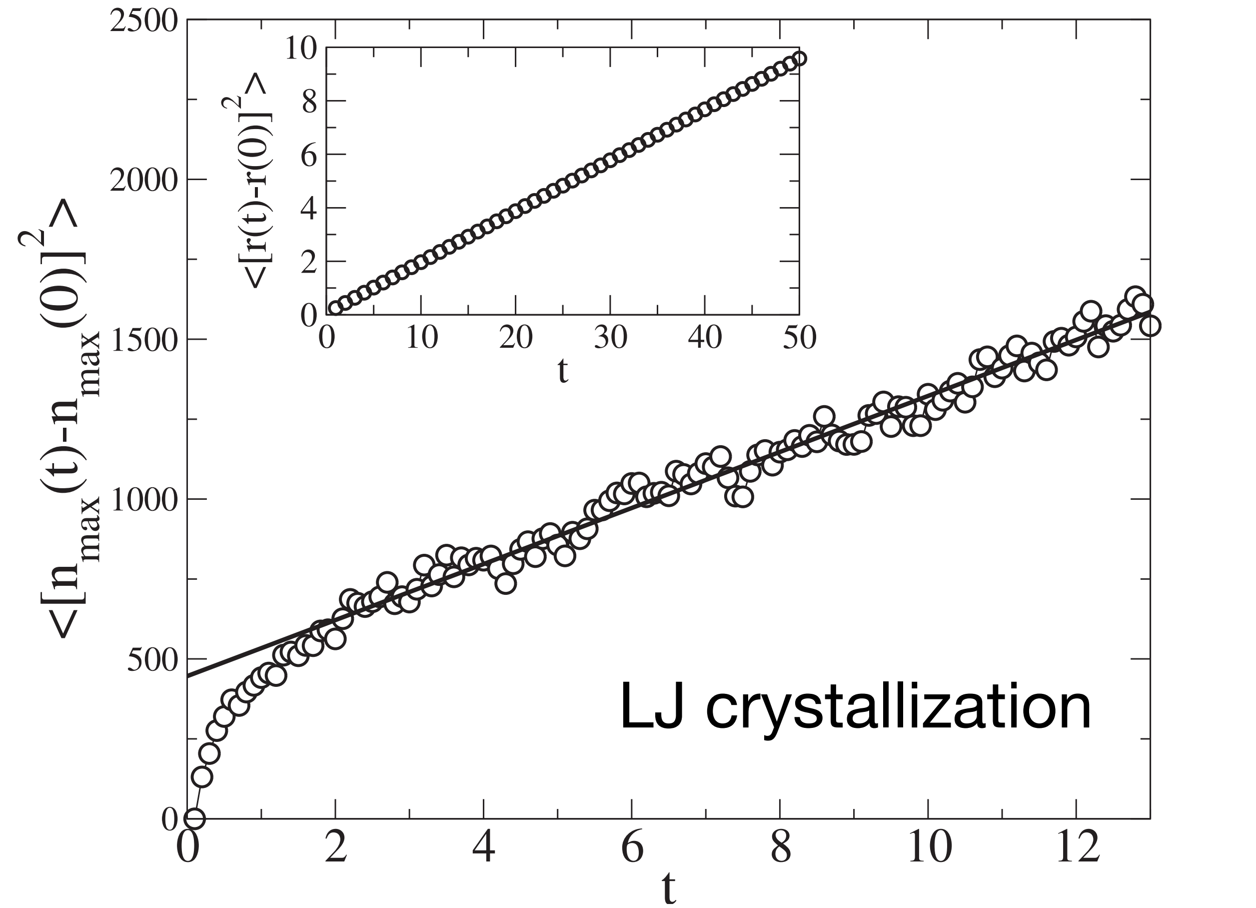


FIG. 5. Determination of $f_{n^*}^+$ at T=0.58 from the time dependence of size fluctuations of near-critical embryos. Shown is a line of best fit obtained by fitting the data (circles) starting from t=4. Inset: mean squared displacement as a function of t for the metastable liquid, also at T=0.58.

Separately run a MD simulations starting from a configuration containing a cluster of near-critical size.
(S. Auer and D. Frenkel, J. Chem. Phys. 120, 3015, 2004)

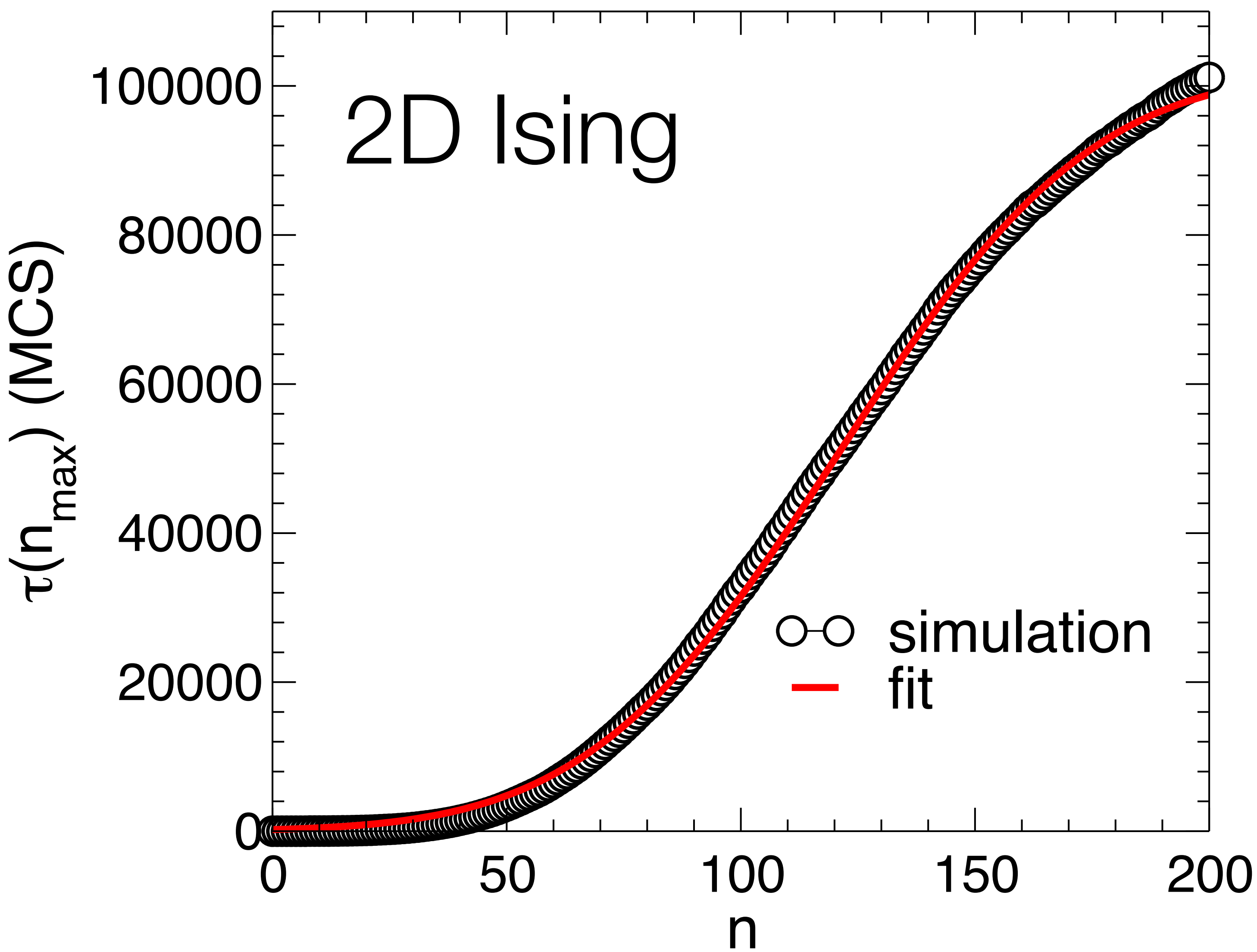
MFPT approach gives full kinetic info

- Prediction for $\tau(n_{\max})$:

$$\tau(n_{\max}) = \frac{1 + \operatorname{erf}[c(n_{\max} - n^*)]}{2JV}$$

- The rate J is immediately available from the fit.
- $Z = c/\sqrt{\pi}$
- $f_c^+ = B(x)/\tau'(x)$, where

$$B(x) = -\frac{1}{P_{\text{st}}(x)}\left[\int_x^b P_{\text{st}}(x')\,\mathrm{d}x' - \frac{\tau(b) - \tau(x)}{\tau(b)}\right]$$



J. Wedekind, R. Strey, and D. Reguera, J. Chem. Phys. 126, 134103, 2007.
J. Wedekind and D. Reguera, J. Phys. Chem. B 112, 11060, 2008.

MFPT analysis of LJ crystallization

Lundrigan and Saika-Voivod, JCP, 2009

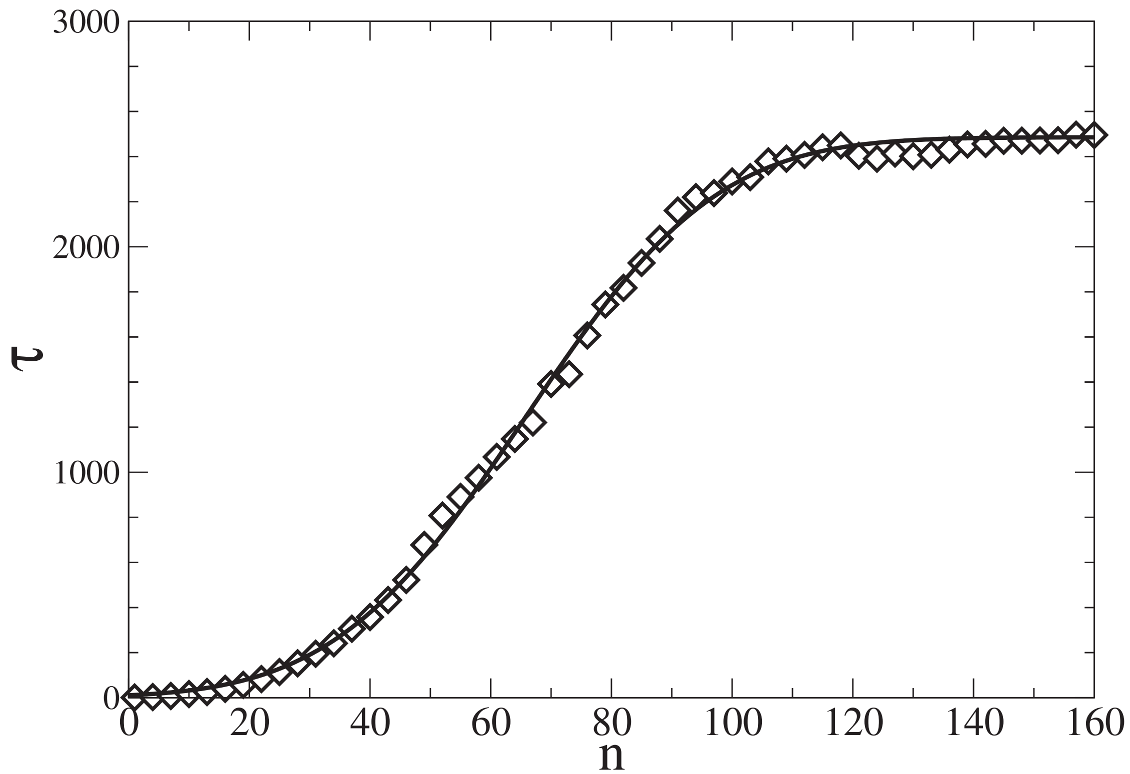


FIG. 3. Plot of mean first-passage times. Plotted are $\tau(n)$ (diamonds), along with a fit of $\tau(n)$ to Eq. (1).

$$\tau(n) = \frac{1}{2JV}\{1 + \mathrm{erf}[c(n - n^*)]\}, \qquad (1)$$

TABLE I. Summary of calculated quantities for T=0.58.

Quantity	Value
N_p	4000
ρ	0.95
n^*_{MFPT}	65 ± 1
n^*	71 ± 1
$\beta\Delta F(n^*)$	15.74 ± 0.25
$f^+_{n^*}$	43 ± 3
D	0.0317
Z_{MFPT}	0.0158 ± 0.0006
Z_{MC}	0.0175 ± 0.0011
λ	0.55 ± 0.03
J	$(9.0 \pm 0.7) \times 10^{-8}$
J_{MFPT}	$(9.4 \pm 0.3) \times 10^{-8}$
J_{CNT}	$(10 \pm 3) \times 10^{-8}$

Summary:
Comparison of biased sampling and MFPT analysis

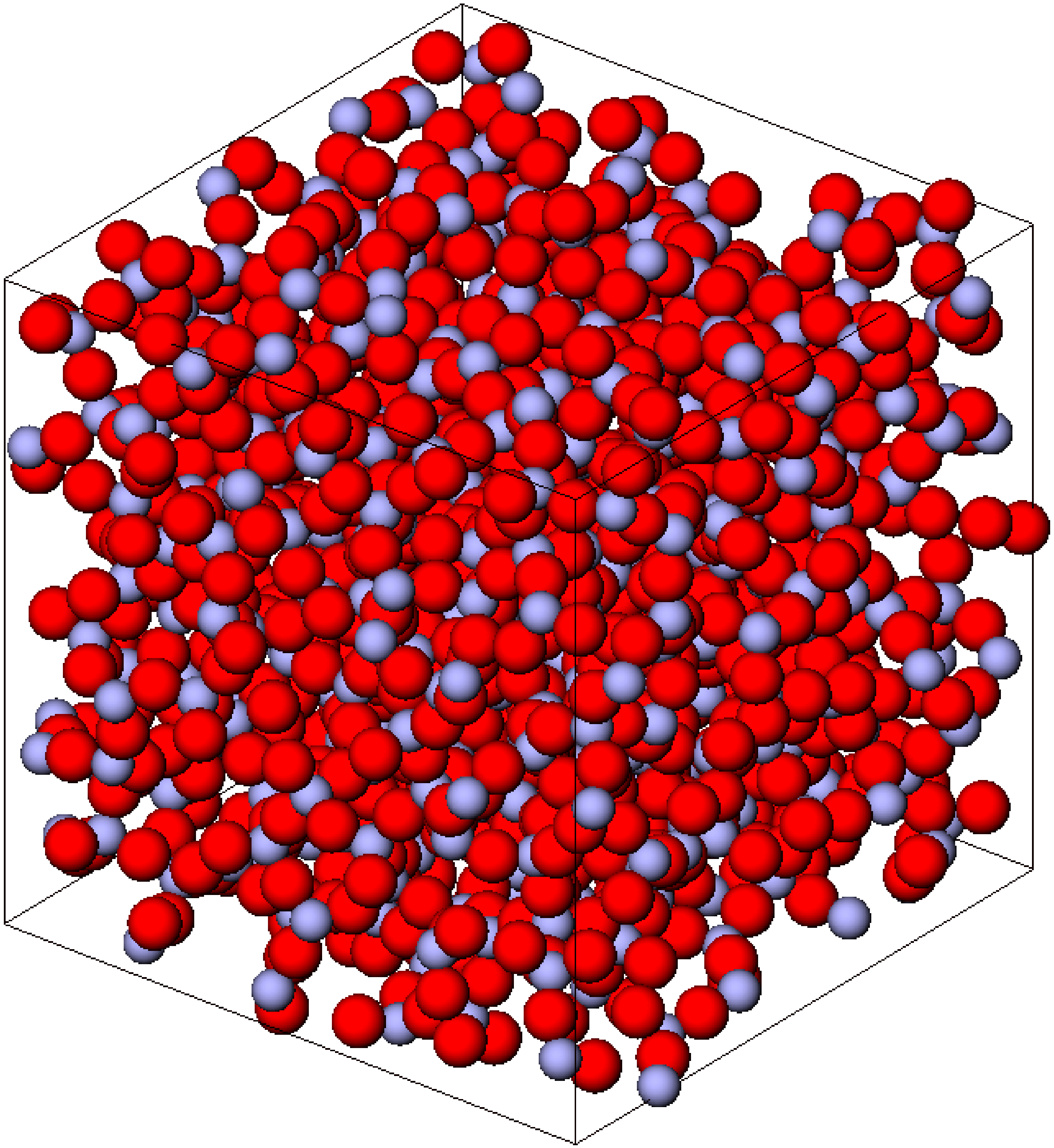
If you cannot simulate nucleation directly:

- Use biased sampling to find ΔG^* and n^*.
- Separate runs required to find f_c^+.
- Obtain Z either from shape of $\Delta G(n)$ or by finding $\Delta\mu$.

If you can observe nucleation directly:

- MFPT is a robust way to analyze both thermodynamics and kinetics.
- Use caution when barriers get small.

MD simulations of BKS silica



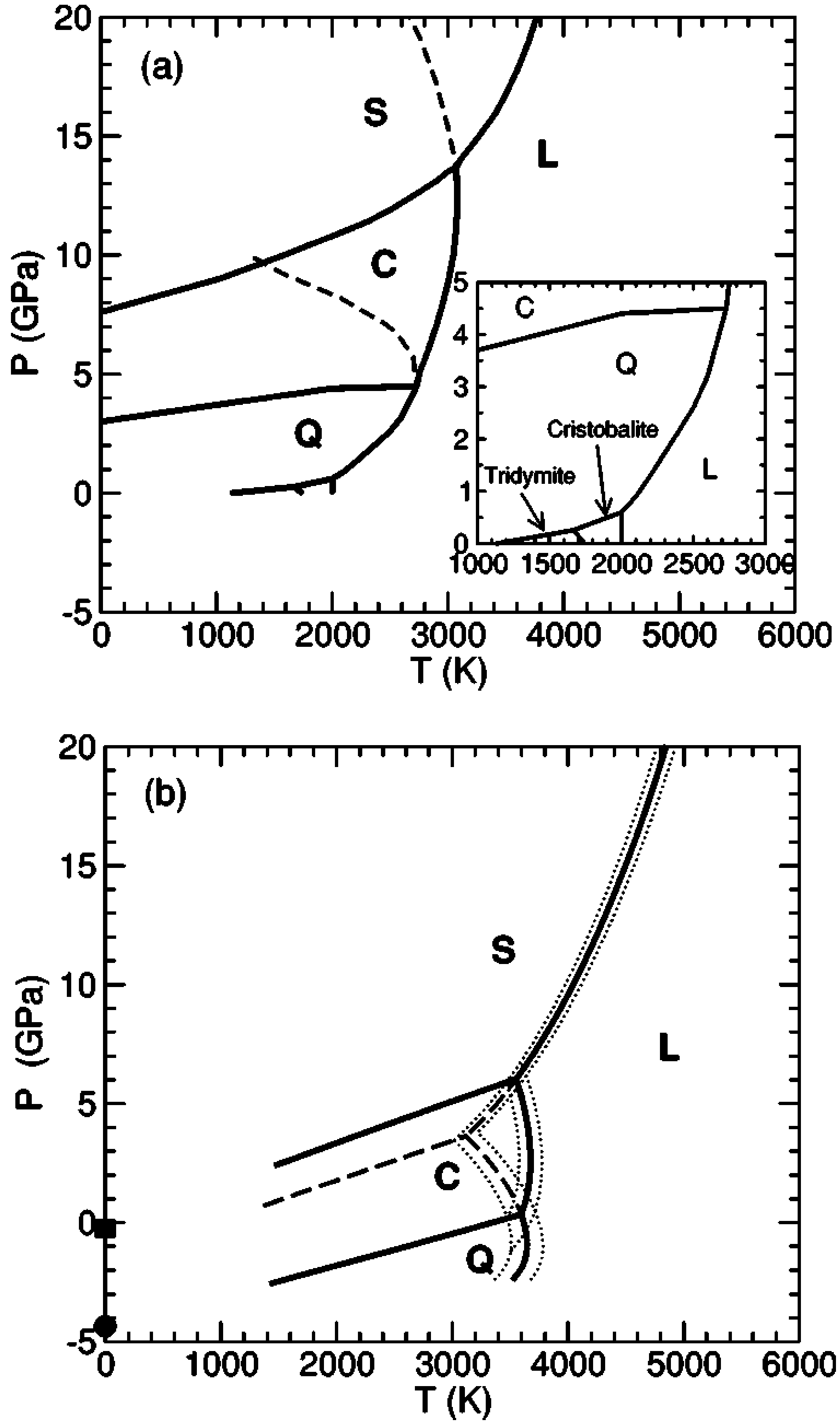
- BKS silica pair potential: Van Beest, et al., 1990
- Charged soft spheres; ignores polarizability, 3-body interactions

$$\phi_{ij}(r) = \frac{1}{4\pi\varepsilon}\frac{q_i q_j}{r} + A_{ij}e^{-B_{ij}r} + \frac{C_{ij}}{r^6}$$

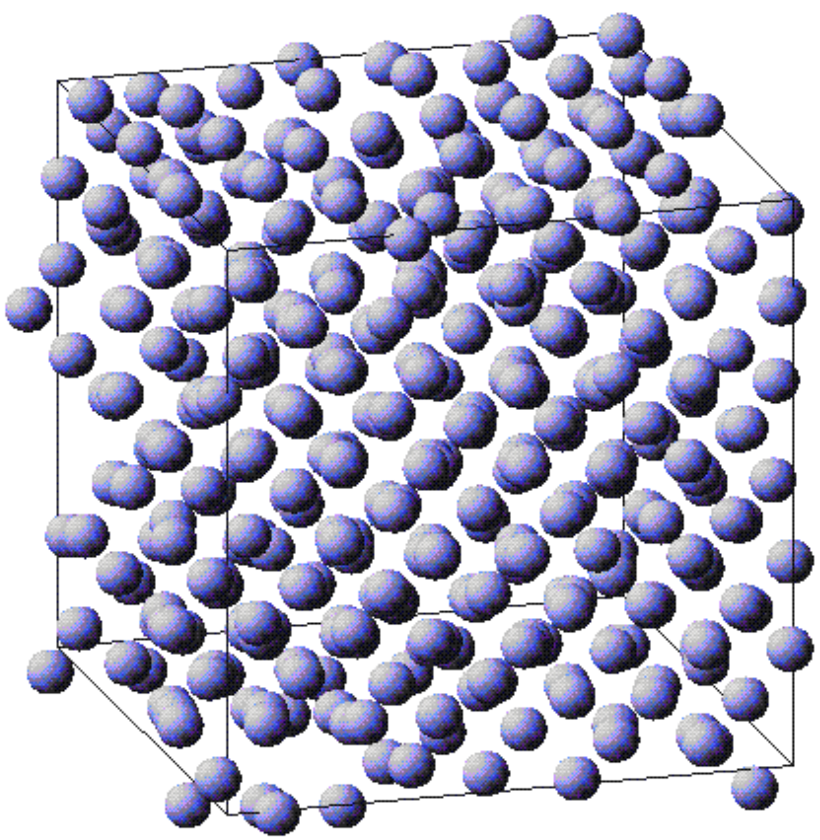
- Long range forces evaluated via Ewald method.
- Plus we add switching function to real-space part of potential.
- Constant (N,V,E) molecular dynamics simulations
- 1332 ions (888 O, 444 Si)
- See Saika-Voivod, et al., PRE (2004) for basic simulation details.

Phase diagram of BKS silica (P-T plane)

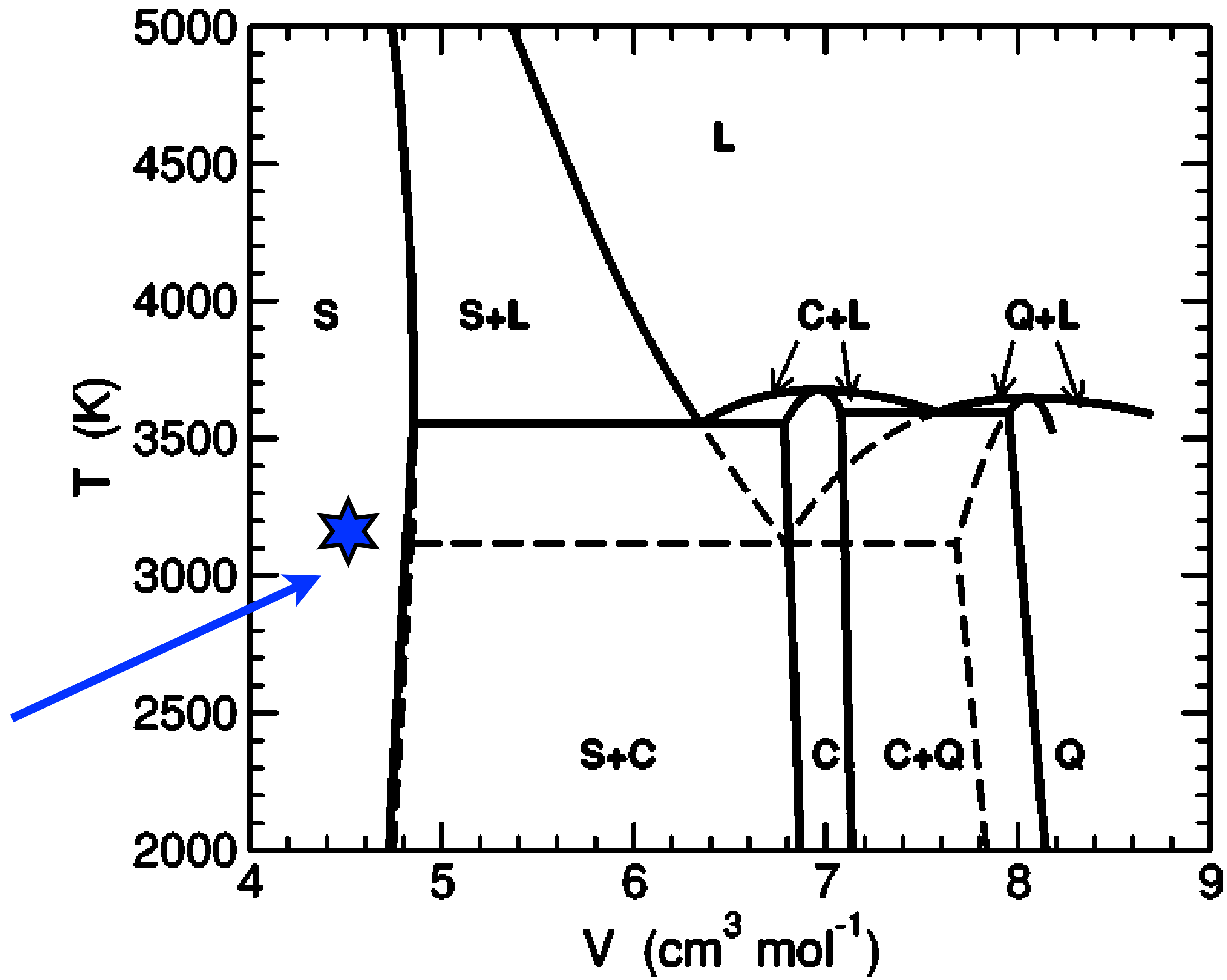
Saika-Voivod, Sciortino, Grande, PHP, PRE 68, 011505 (2003)



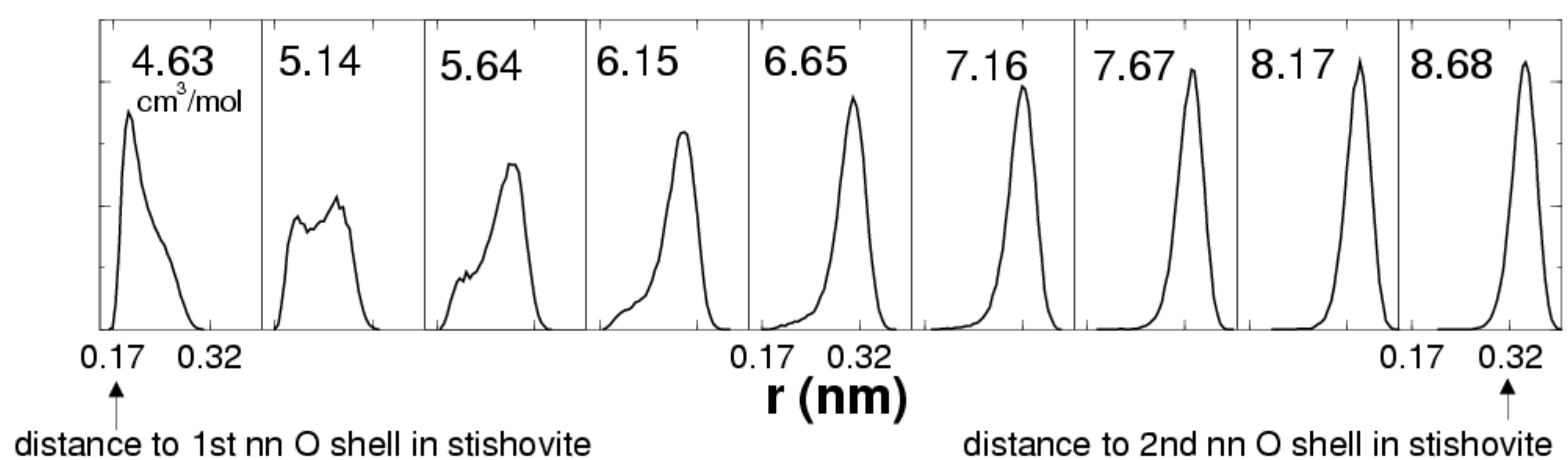
Phase diagram of BKS silica (T-V plane)



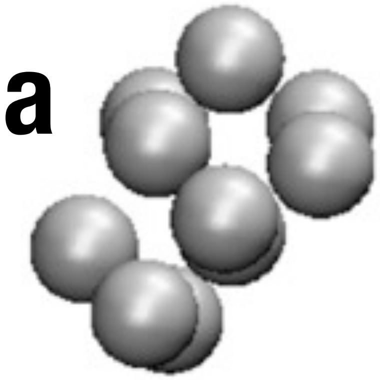
stishovite crystallized from liquid



distribution of distance to sixth nn O of SI atoms in liquid at T=3000 K



Stishovite crystallization in BKS silica



Saika-Voivod, PHP, Bowles, JCP 124, 224709 (2006)

- In CNT, the nucleation rate is

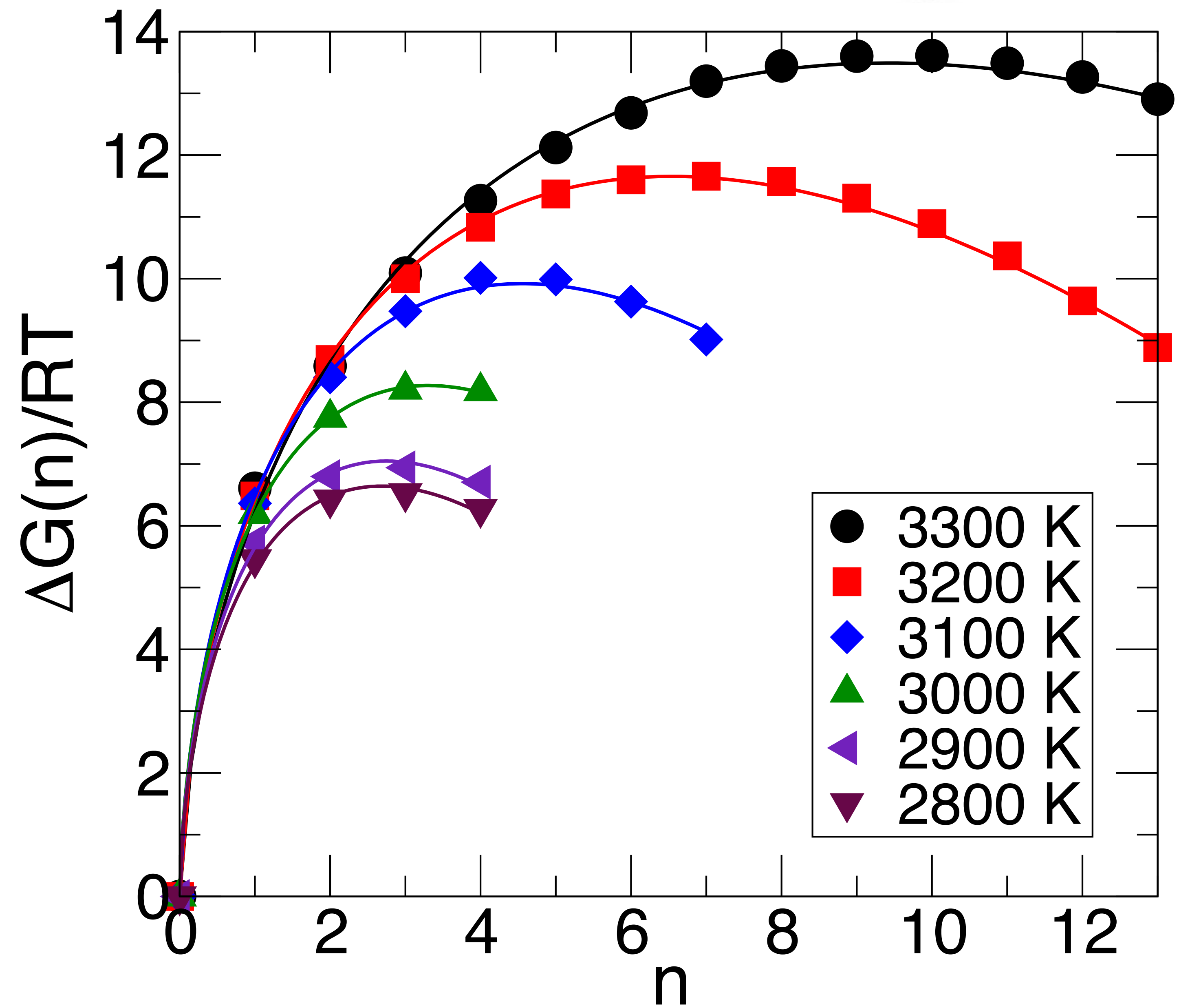
$$J = K \exp(-\beta \Delta G^*)$$

- $K = \rho_n Z f_c^+$
- ρ_n is the number density of the particles.
- Z is the Zeldovich factor:

$$Z = \sqrt{\frac{\beta|\Delta\mu|}{6\pi n^*}}$$

- f_c^+ is the attachment rate of particles to the critical nucleus, found using,

$$f_c^+ = \frac{\langle [n^*(t) - n^*(0)]^2 \rangle}{2t}$$



curves are fits to CNT form:

$$\Delta G(n) = -|\Delta\mu| n + a n^{2/3}$$

Stishovite crystallization in BKS silica

Saika-Voivod, PHP, Bowles, JCP 124, 224709 (2006)

- In CNT, the nucleation rate is

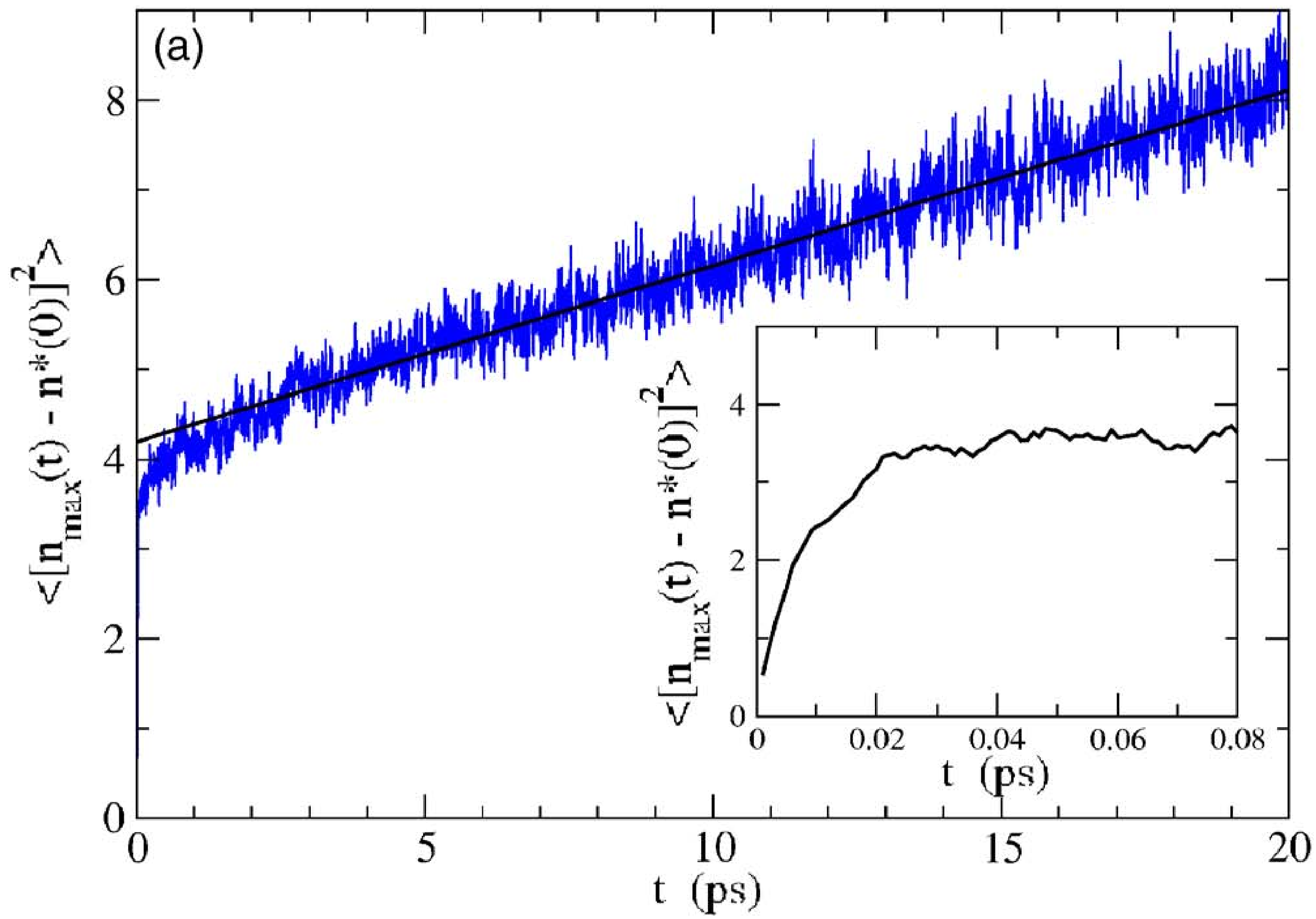
$$J = K \exp(-\beta \Delta G^*)$$

- $K = \rho_n Z f_c^+$
- ρ_n is the number density of the particles.
- Z is the Zeldovich factor:

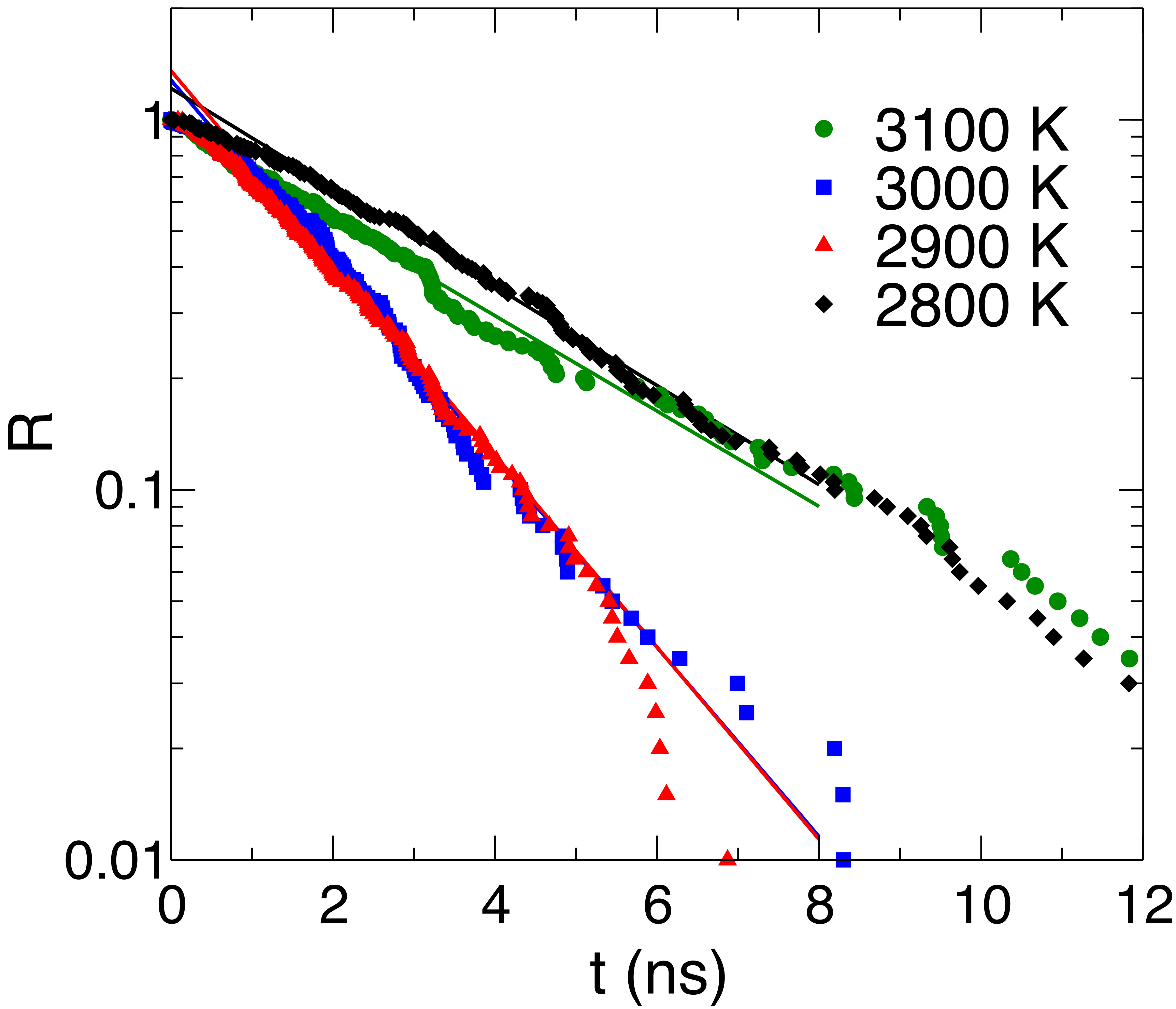
$$Z = \sqrt{\frac{\beta |\Delta\mu|}{6\pi n^*}}$$

- f_c^+ is the attachment rate of particles to the critical nucleus, found using,

$$f_c^+ = \frac{\langle [n^*(t) - n^*(0)]^2 \rangle}{2t}$$



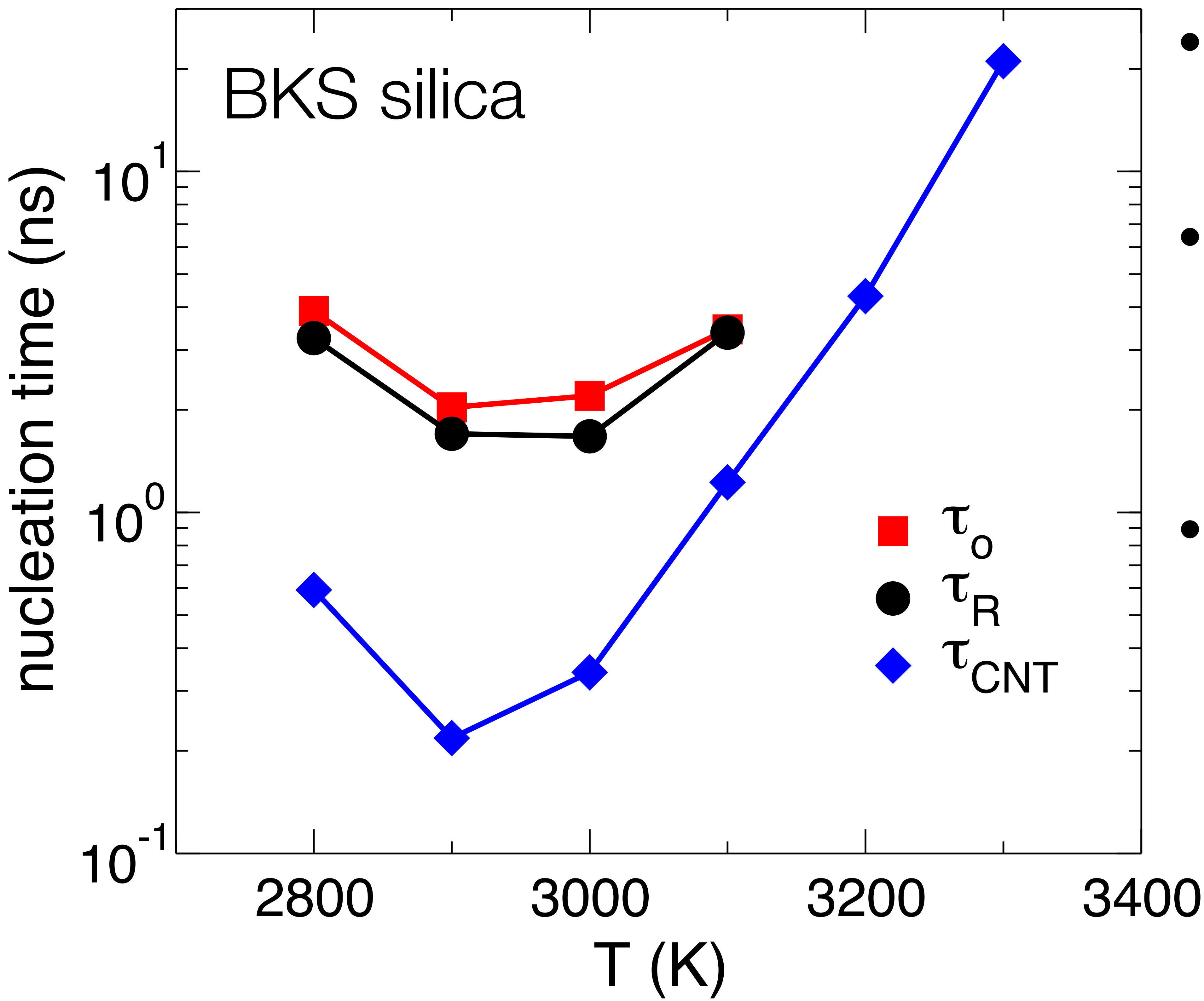
Evaluating the mean nucleation time



- 200 runs at each T
- R is the number of runs remaining un-nucleated after time t.

- slope gives system nucleation rate (JV)
- characteristic nucleation time $\tau_R = (JV)^{-1}$

Crystal nucleation times vs T



- τ_o=average of latest time that the max cluster size was 0
- τ_R found from rates, with definition of nucleation time as last time that max cluster size was 0.
- τ_{CNT} is nucleation time evaluated based on CNT.

Lecture 2
Interplay of glassy dynamics and crystal nucleation on approaching Kauzmann's entropy catastrophe

Peter H. Poole
St. Francis Xavier University
Antigonish, Nova Scotia, Canada

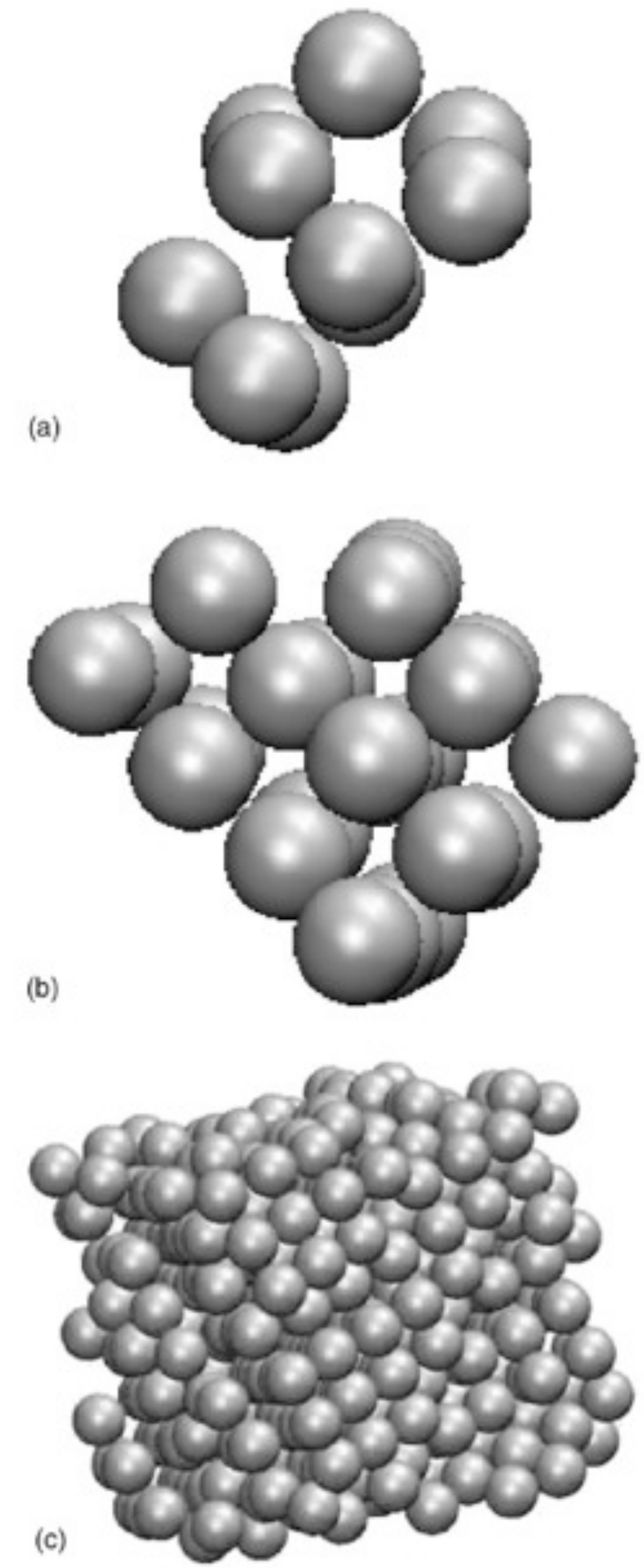
School on Glass Formers and Glasses - Bengaluru - January, 2010

Outline

- Kauzmann's 1948 proposal for resolving his famous paradox: that crystal nucleation prevents the supercooled liquid from reaching the entropy catastrophe

- Tanaka's 2003 insight: breakdown of the Stokes-Einstein relation makes this scenario a real possibility

- Testing this scenario in simulations of BKS silica



I. Saika-Voivod, R.K. Bowles and PHP, Phys Rev Lett **103**, 225701 (2009).

Collaborators

New work with...

Ivan Saika-Voivod
Department of Physics and Physical Oceanography
Memorial University of Newfoundland, St. John's, Newfoundland

Richard K. Bowles
Department of Chemistry, University of Saskatchewan
Saskatoon, Saskatchewan

Builds on earlier results with...

Francesco Sciortino
Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia
Università di Roma La Sapienza, Rome

Kauzmann's Paradox

- A thermodynamic problem (the impending entropy catastrophe of supercooled liquids) is not resolved by appealing to a dynamic phenomenon (the glass transition).

THE NATURE OF THE GLASSY STATE AND THE BEHAVIOR OF LIQUIDS AT LOW TEMPERATURES

WALTER KAUZMANN

Department of Chemistry, Princeton University, Princeton, New Jersey

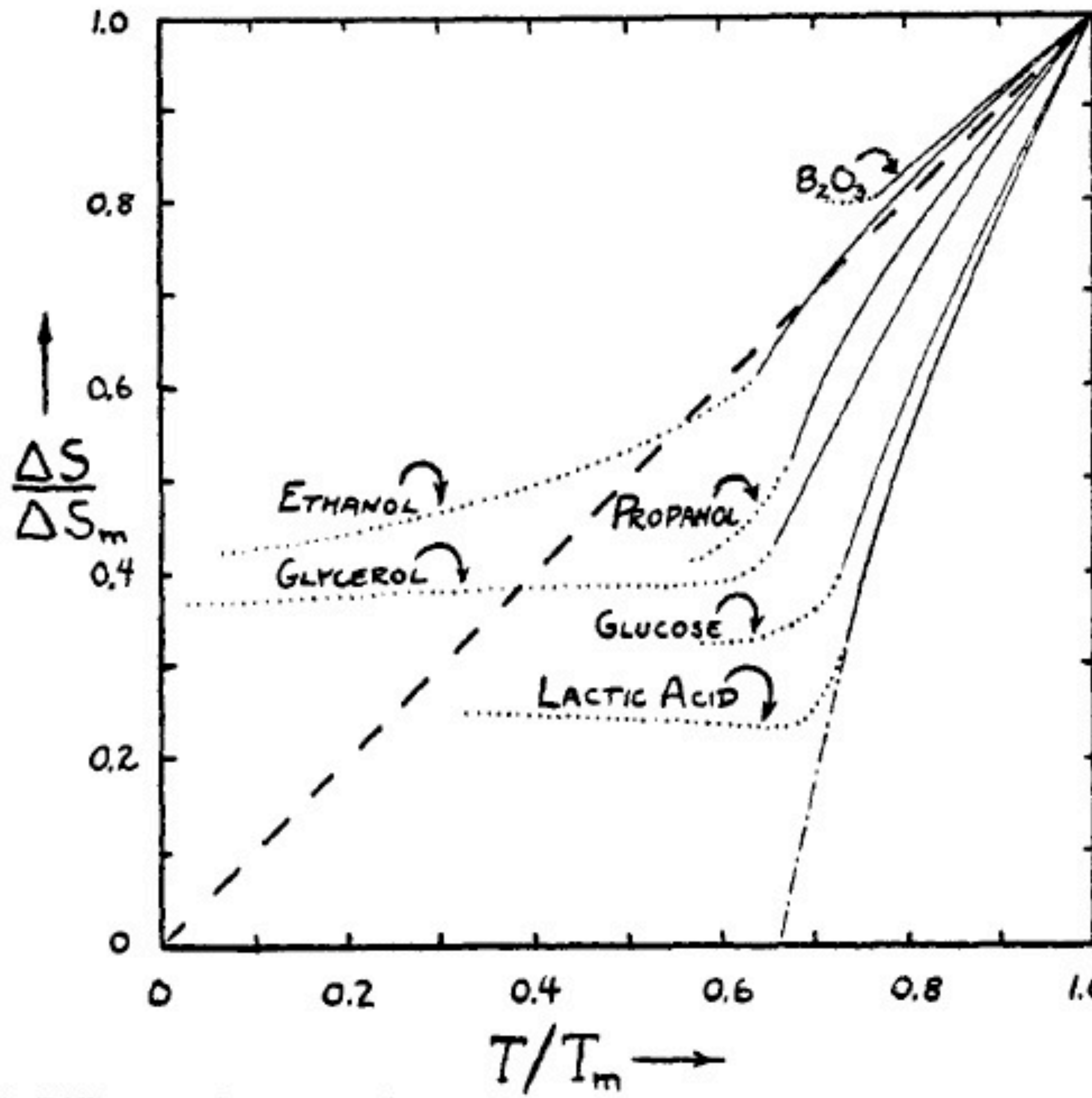
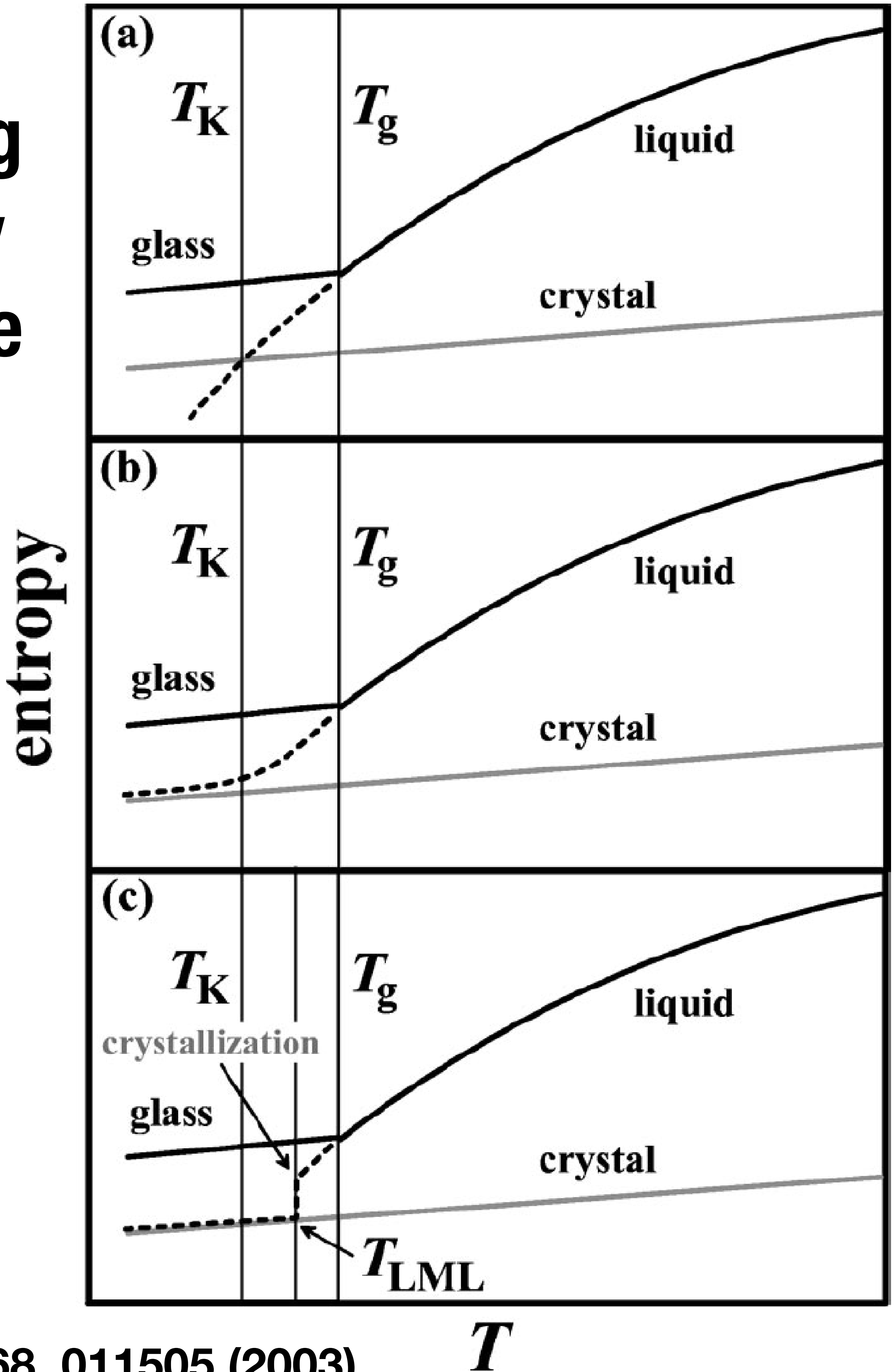


FIG. 4. Differences in entropy between the supercooled liquid and crystalline phases. Abscissa: as in figure 3. Ordinate: difference in entropy expressed as fraction of the entropy of fusion.

W. Kauzmann,
Chem. Rev. 43, 219 (1948)

Scenarios for avoiding the entropy catastrophe



(a) Ideal glass transition at T_K

(b) Fragile-to-strong crossover (first-order or continuous)

(c) Crystallization occurs before T_K can be reached

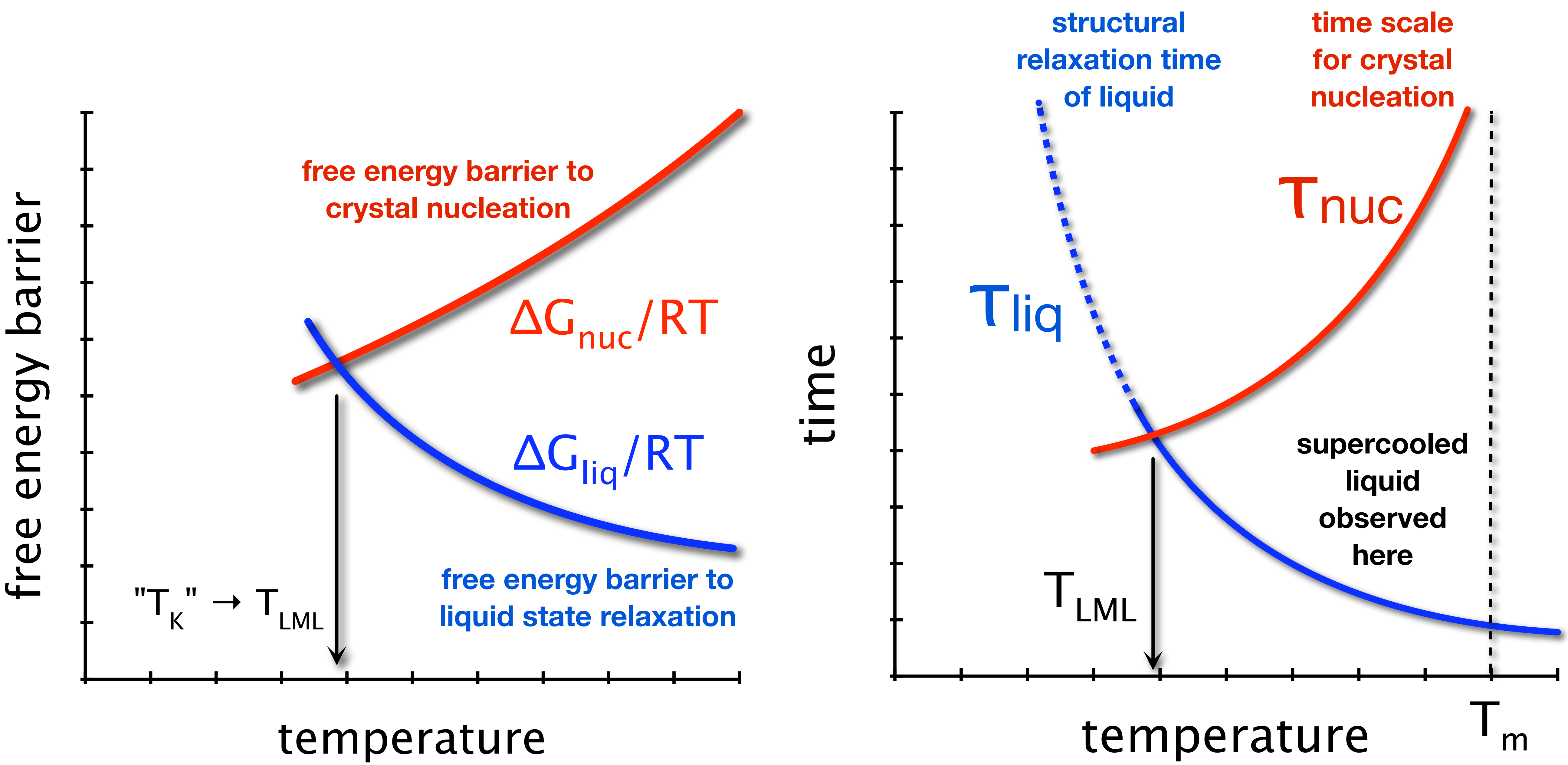
Fig. 1 from H. Tanaka, PRE 68, 011505 (2003)

W. Kauzmann, Chem. Rev. 43, 219 (1948)...from pages 246-7:

Throughout this discussion we have been making implicit use of the idea that there are two kinds of metastability possible in liquids: *viz.*, that shown by a normal supercooled liquid with respect to the crystal, and that shown by a glass with respect to the normal supercooled liquid. Now metastability implies the existence of a free energy barrier between the metastable state and the normal state. In this case the first kind of metastability arises chiefly from the free energy barrier preventing the formation of crystal nuclei (23, 92, 102), while we have shown that the second kind of metastability is made possible by the free energy barriers which impede the motions of molecules from one equilibrium position in the liquid to another. As the temperature is decreased the height of the first kind of barrier generally decreases very markedly (see Appendix B) while the height of the second kind increases (see table 4). Suppose that when the temperature is lowered a point is eventually reached at which the free energy barrier to crystal nucleation becomes reduced to the same height as the barriers to the simpler motions. (This assumption is shown to be plausible in Appendix B and in Section III,E, below.) At such temperatures the liquid would be expected to crystallize just as rapidly as it changed its typically liquid structure to conform to a temperature or pressure change in its surroundings. It would then become operationally meaningless to speak of a metastable non-vitreous liquid as distinguished from a glass; the two kinds of metastability would merge.

Let us denote by T_k the temperature at which the two kinds of barriers become equal.

Kauzmann's resolution of Kauzmann's paradox



T_{LML} = "lower metastable limit" for liquid state

For $T<T_{LML}$ crystal nucleates before liquid equilibrates

Kauzmann (1948):

- At T_{LML}, crossing the barrier to crystal nucleation will be as likely as crossing the barriers associated with liquid-state structural relaxation
- Below T_{LML}, the liquid cannot be observed in equilibrium, because crystal nucleation will occur before internal equilibrium can be attained.

Classical nucleation theory (CNT) seems to suggest this won't happen...

In CNT the nucleation rate is given by

$$J = K \exp\left(-\frac{\Delta G(n^*)}{kT}\right)$$

where

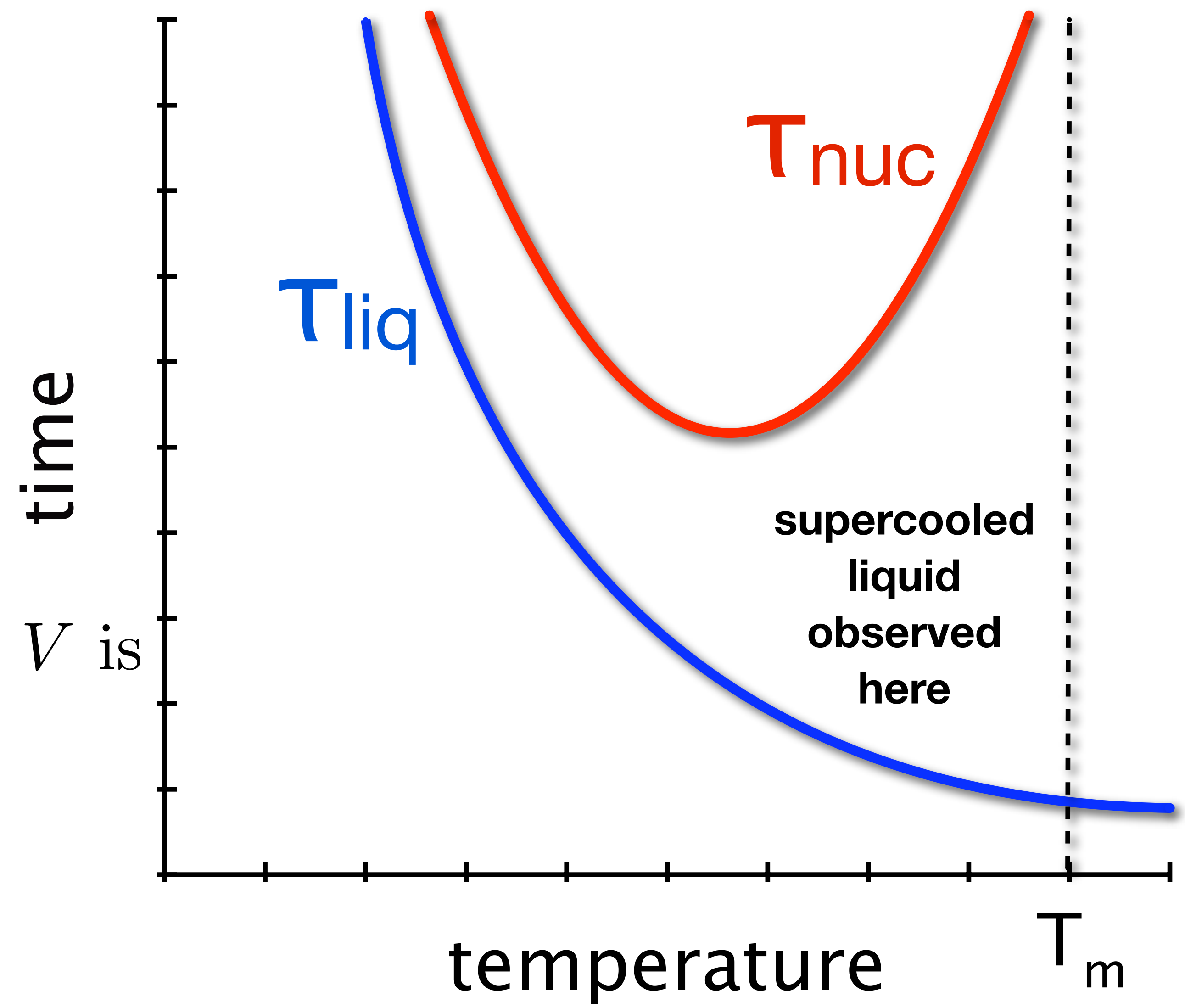
$$K = 24\, D\, \rho_n\, Z\, n^{*\frac{2}{3}}\, \lambda^{-2}$$

and

$$Z = \sqrt{\frac{|\Delta\mu|}{6\pi kTn^*}}$$

Nucleation time for a system of volume V is

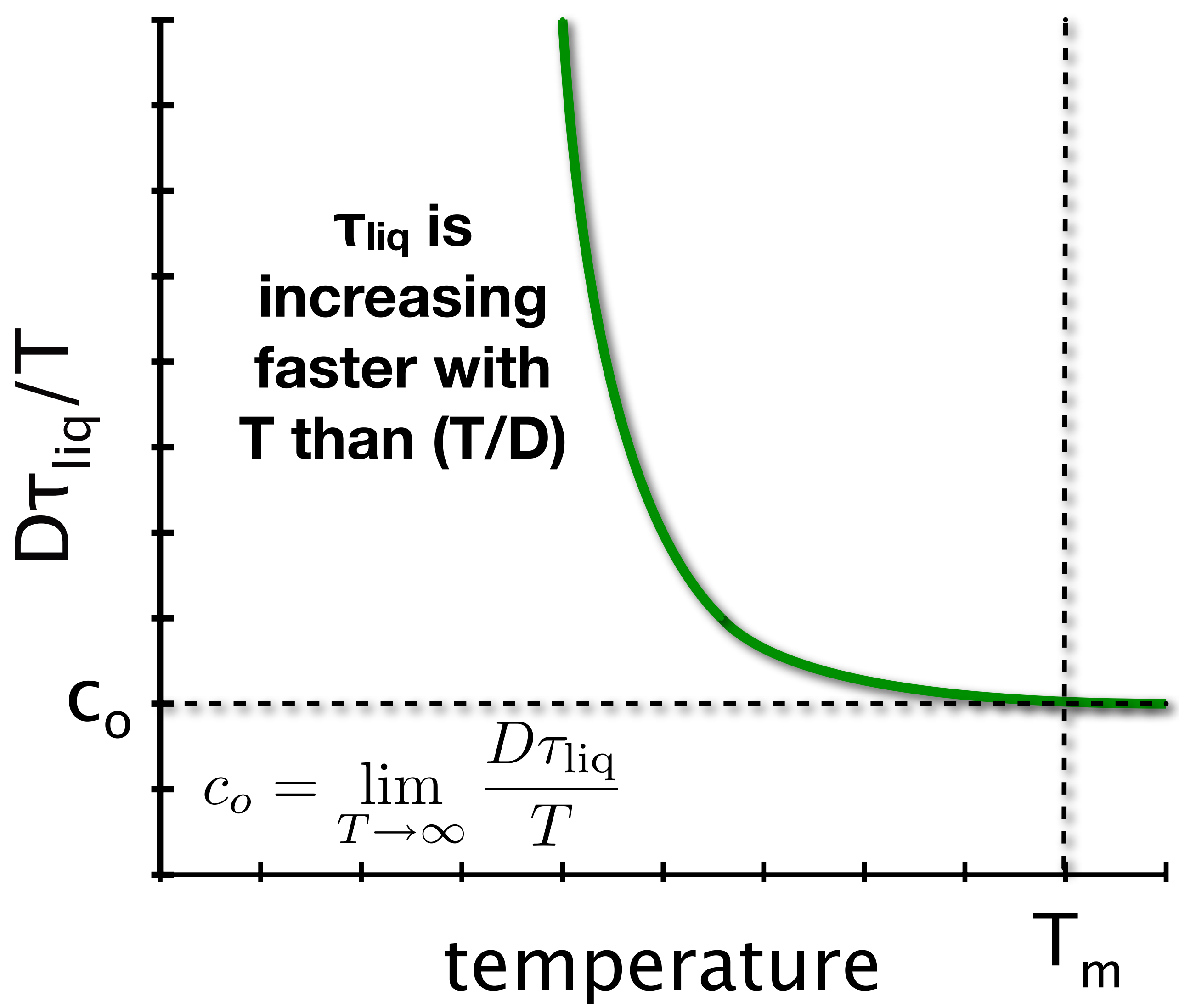
$$\tau_{\text{nuc}} = (JV)^{-1} = \frac{A}{D} \exp\left(\frac{\Delta G(n^*)}{kT}\right)$$

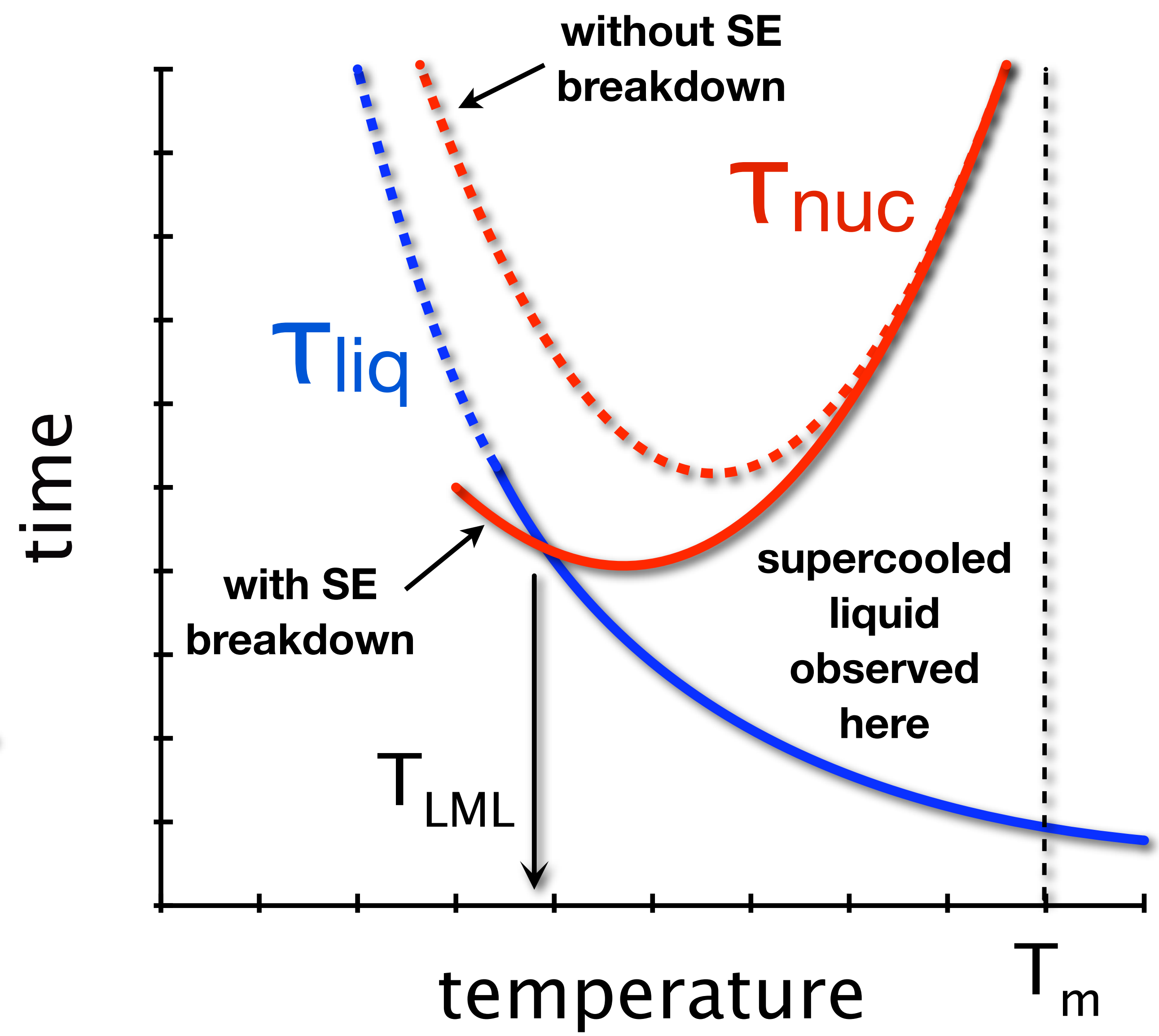


As long as $D^{-1} \sim \tau_{\text{liq}}$ then $\tau_{\text{nuc}} > \tau_{\text{liq}}$

...which means no T_{LML}.

...but if the Stokes-Einstein (SE) relation breaks down, T_{LML} can exist, within the CNT framework





Stokes-Einstein relation...

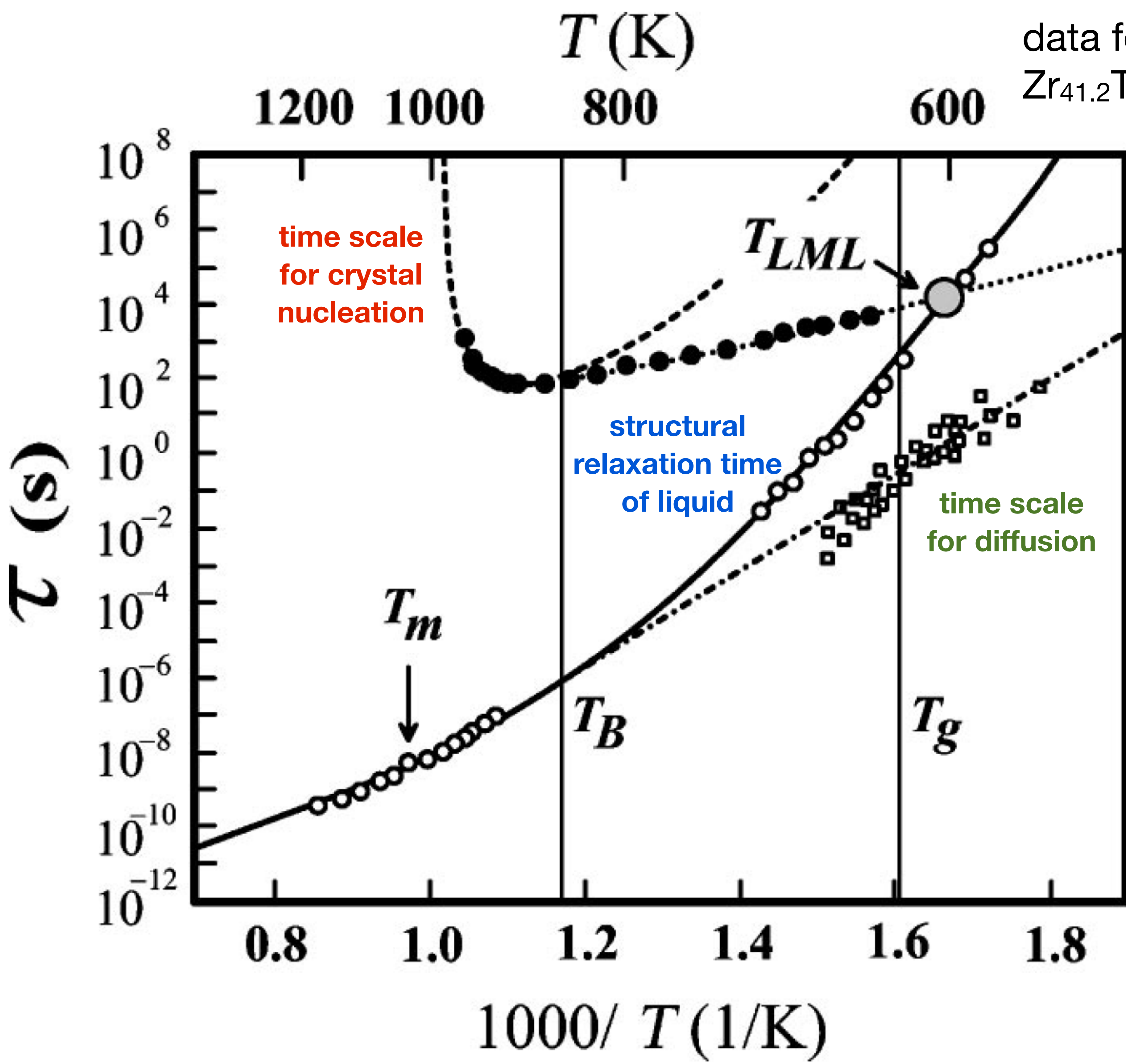
$$\frac{D\eta}{T} = \text{const}$$

we assume...

$$\tau_{liq} \sim \eta$$

$$\tau_{nuc} = \frac{A}{D} \exp\left(\frac{\Delta G(n^*)}{kT}\right)$$

H. Tanaka, PRE 68, 011505 (2003)

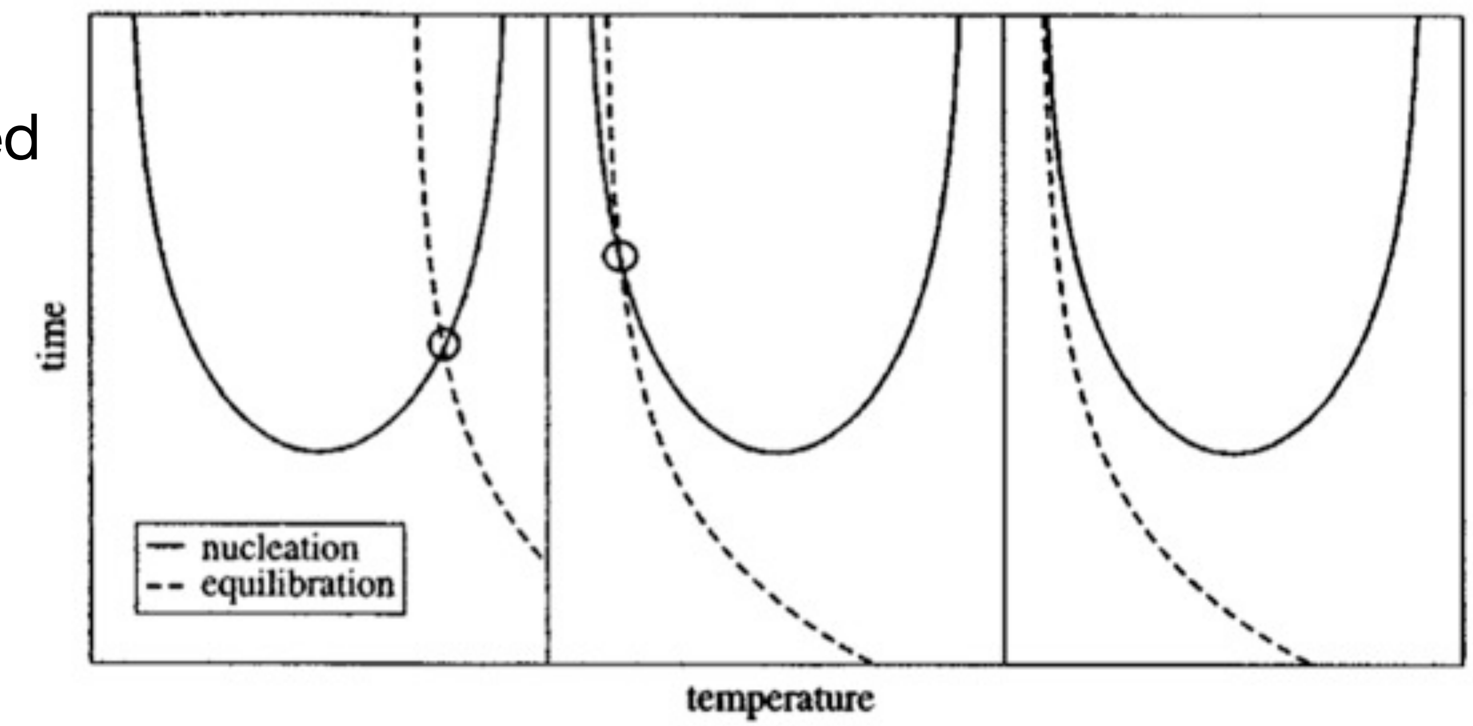


data for the metallic glass former $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$

from A. Masuhr, et al., Phys. Rev. Lett. 82, 2290 (1999)

Other recent work on stability limits of supercooled liquids...

- A. Cavagna and coworkers: “kinetic spinodal temperature” for supercooled liquids...
  - EPL 61, 74 (2003)
  - JCP 118, 6974 (2003)
  - PRL 95, 115702 (2005)

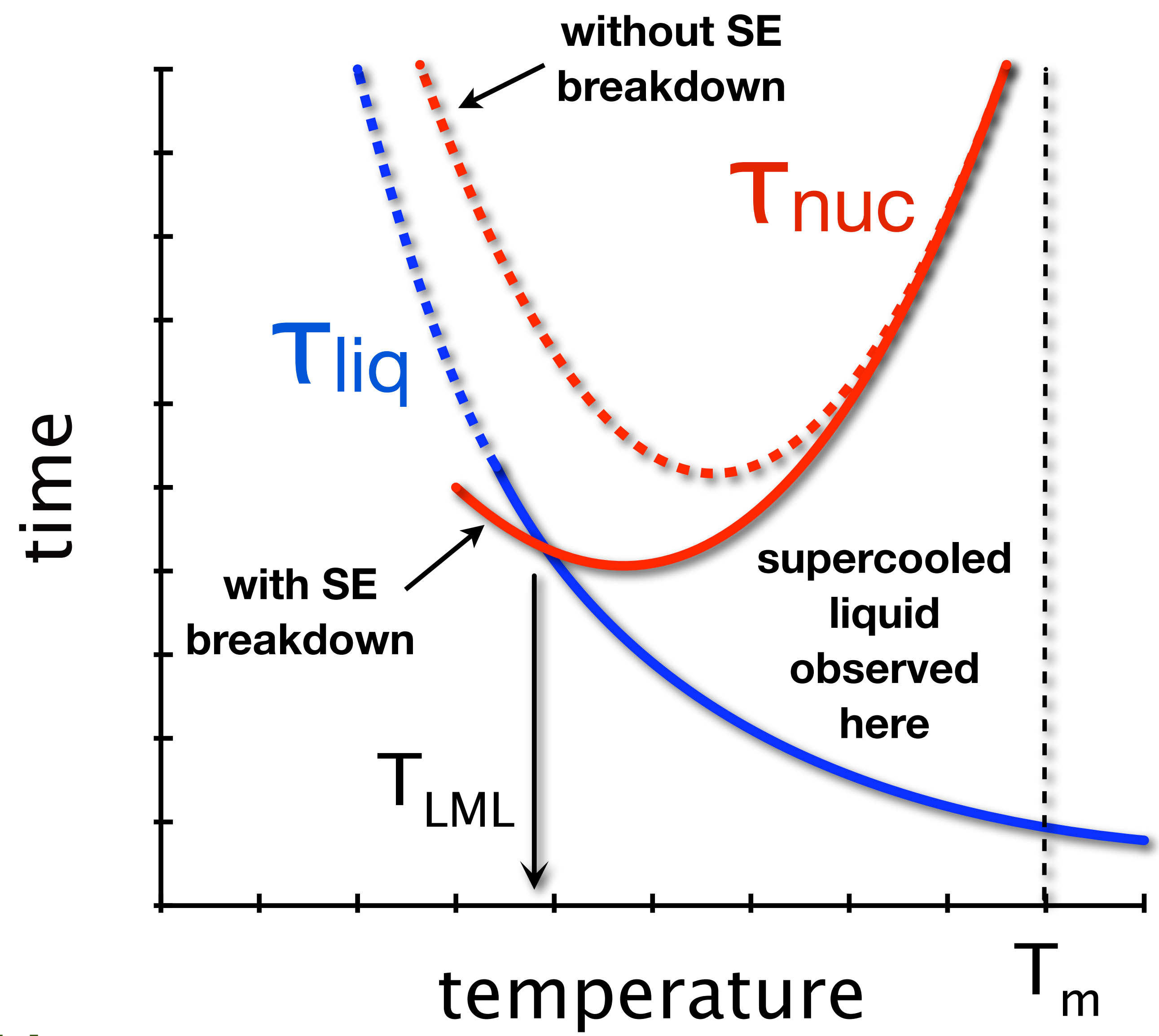


- Spinodal-like crystal nucleation in deeply supercooled LJ liquid...
  - Trudu, Donadio and Parrinello, PRL 97, 105701 (2006)
  - Wang, Gould and Klein, PRE 76, 031604 (2007)

- Stability limits for crystal nucleation in supercooled gold nanoclusters...
  - Mendez-Villuendas, Saika-Voivod and Bowles, JCP, 127, 154703 (2007)

What do we need to study the physics of T_{LML} in simulations?

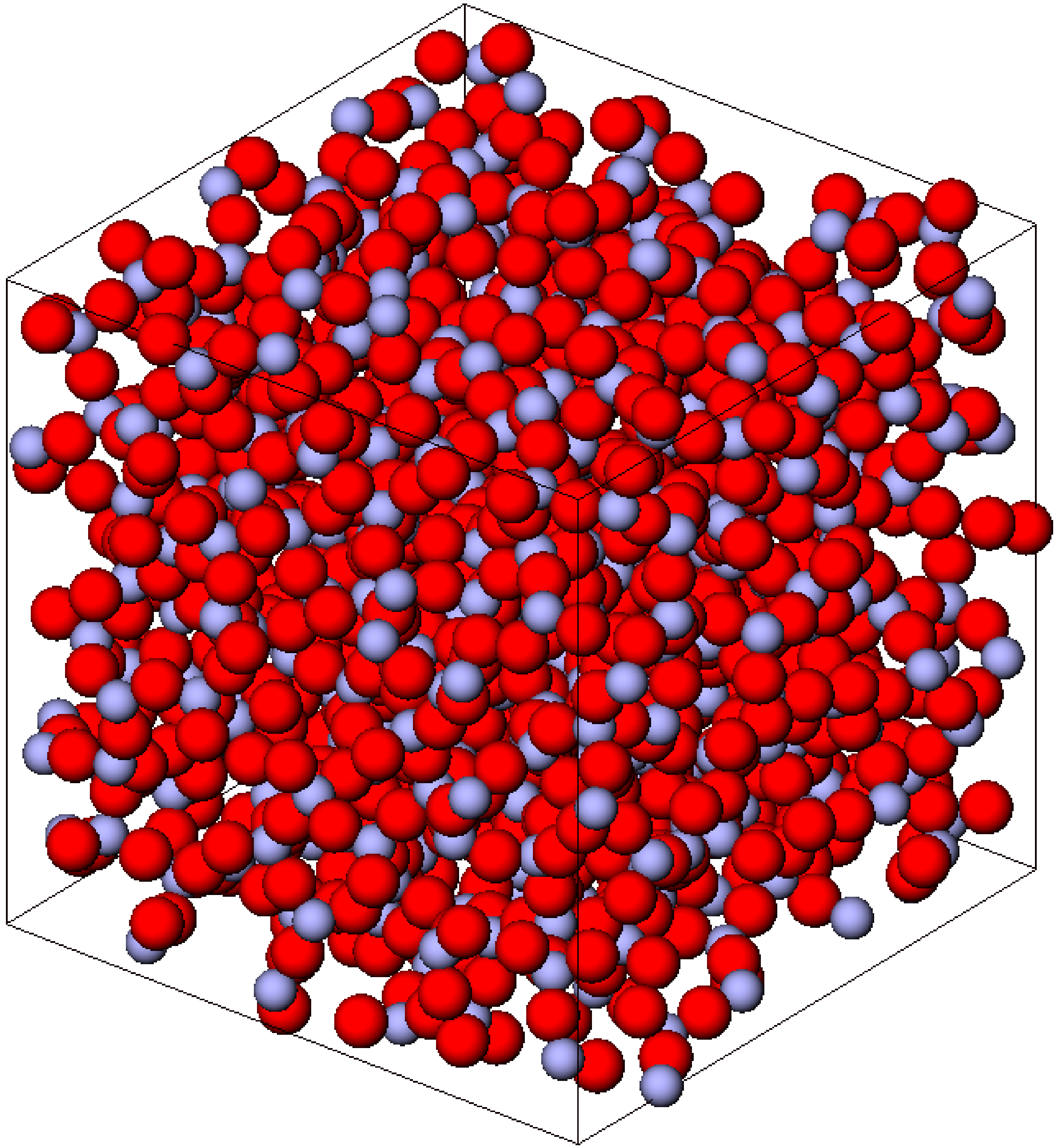
- A system which nucleates spontaneously, and crosses over from steady-state to transient nucleation...
- ...and that exhibits SE breakdown in the same region of T.



T_{LML} = "lower metastable limit" for liquid state....

- **$T>T_{LML}$ → steady-state nucleation: crystal nucleates within equilibrium liquid**
- **$T<T_{LML}$ → transient nucleation: crystal nucleates before liquid equilibrates**

MD simulations of BKS silica



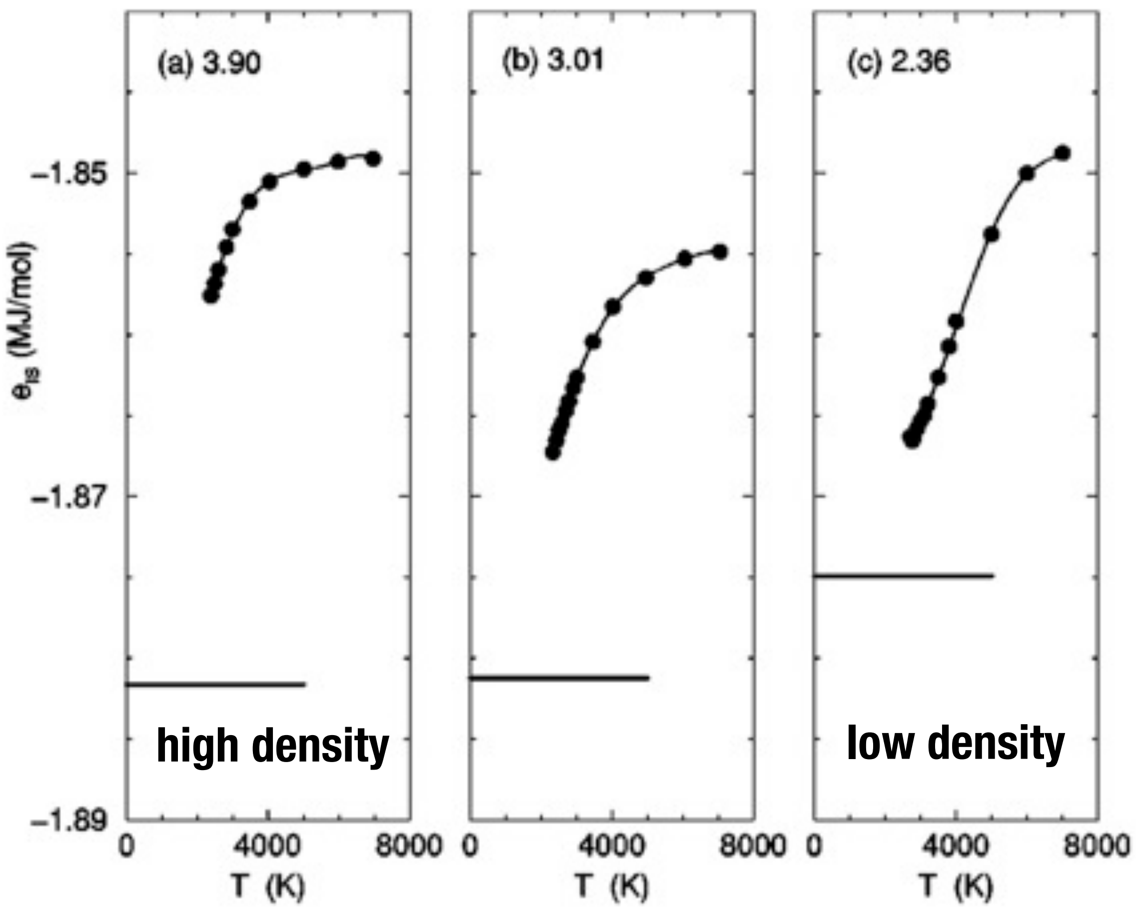
- BKS silica pair potential: Van Beest, et al., 1990
- Charged soft spheres; ignores polarizability, 3-body interactions

$$\phi_{ij}(r) = \frac{1}{4\pi\varepsilon}\frac{q_i q_j}{r} + A_{ij}e^{-B_{ij}r} + \frac{C_{ij}}{r^6}$$

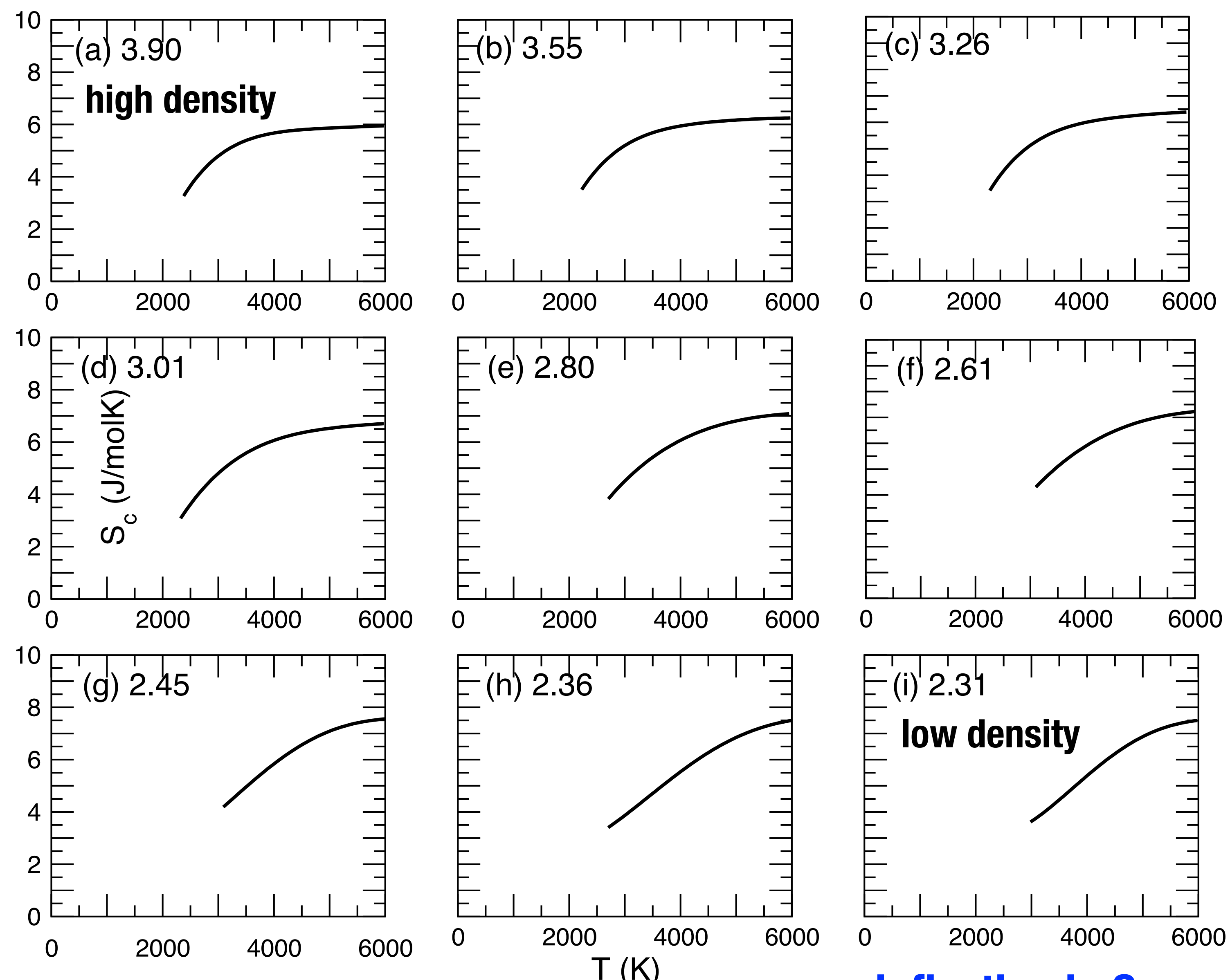
- Long range forces evaluated via Ewald method.
- Plus we add switching function to real-space part of potential.
- Constant (N,V,E) molecular dynamics simulations
- 1332 ions (888 O, 444 Si)
- See Saika-Voivod, et al., PRE (2004) for basic simulation details.

Potential energy landscape and configurational entropy of liquid silica

inherent structure energy, e_{IS}



$S_c(T)$ obtained by evaluating the inherent structure energy, the vibrational entropy, and the total entropy of the liquid, for BKS silica.



Adam-Gibbs relation

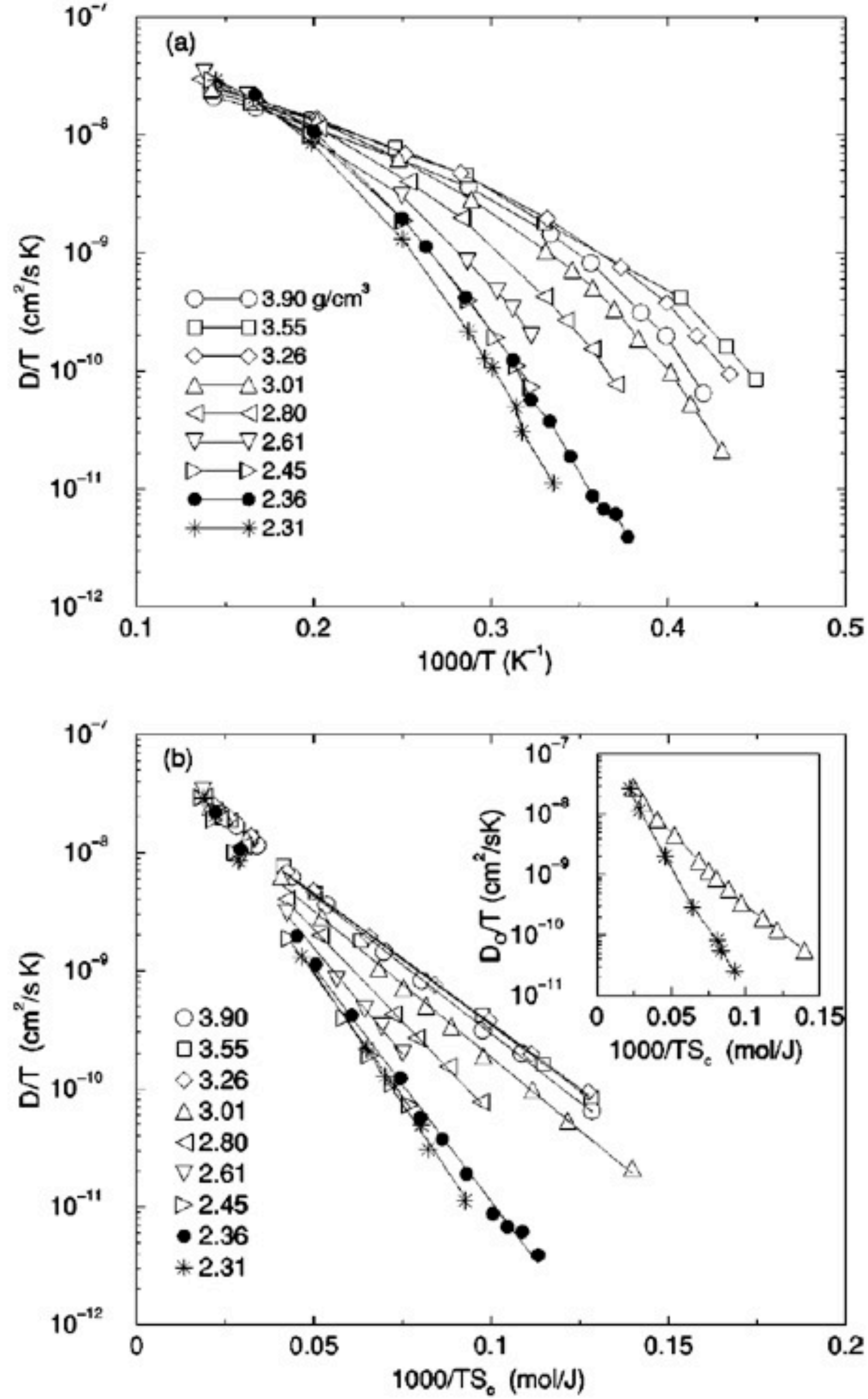
$$\frac{D}{T} = K \exp\left(-\frac{C}{T S_c}\right)$$

inflection in S_c = fragile-to-strong crossover

Saika-Voivod, Poole and Sciortino, Nature, 2001; PRE, 2004.

Test of Adam-Gibbs theory in liquid BKS silica

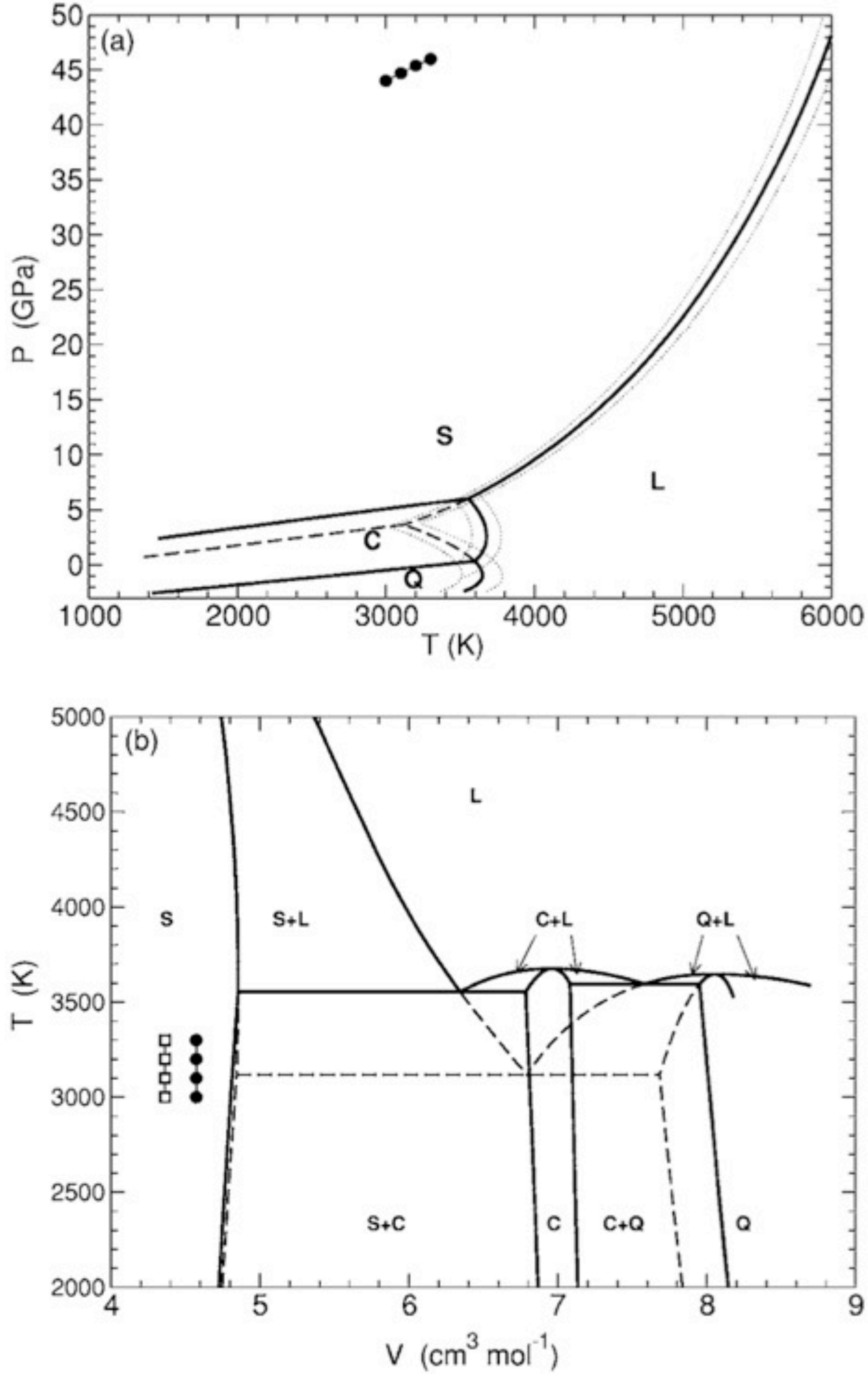
Saika-Voivod, Poole and Sciortino,
Nature, 2001; PRE, 2004.



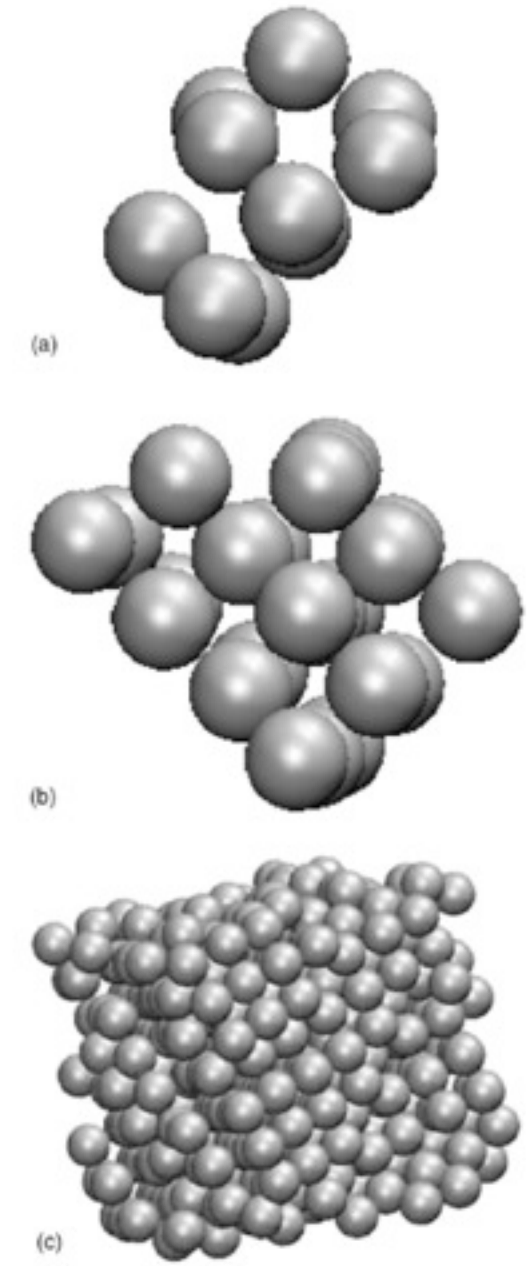
The AG relation is satisfied along isochores, and this gives us the constant “C” in the AG relation at any given density.

$$\frac{D}{T} = K \exp\left(-\frac{C}{TS_c}\right)$$

Supercooled liquid BKS silica spontaneously crystallizes to stishovite at high density



Crystallization occurs at density 4.38 g/cm^3 for T<3200 K

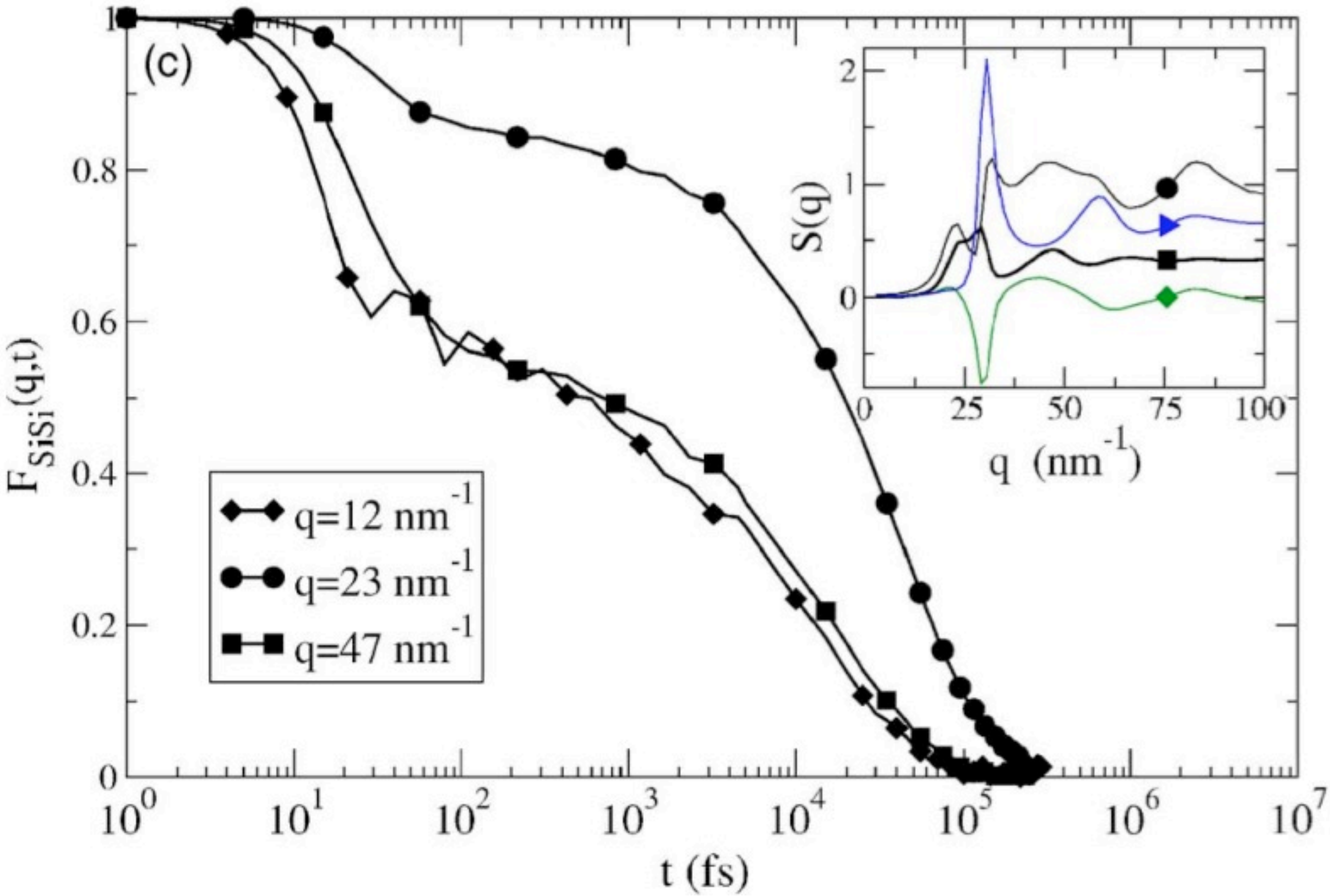


Si atoms only shown

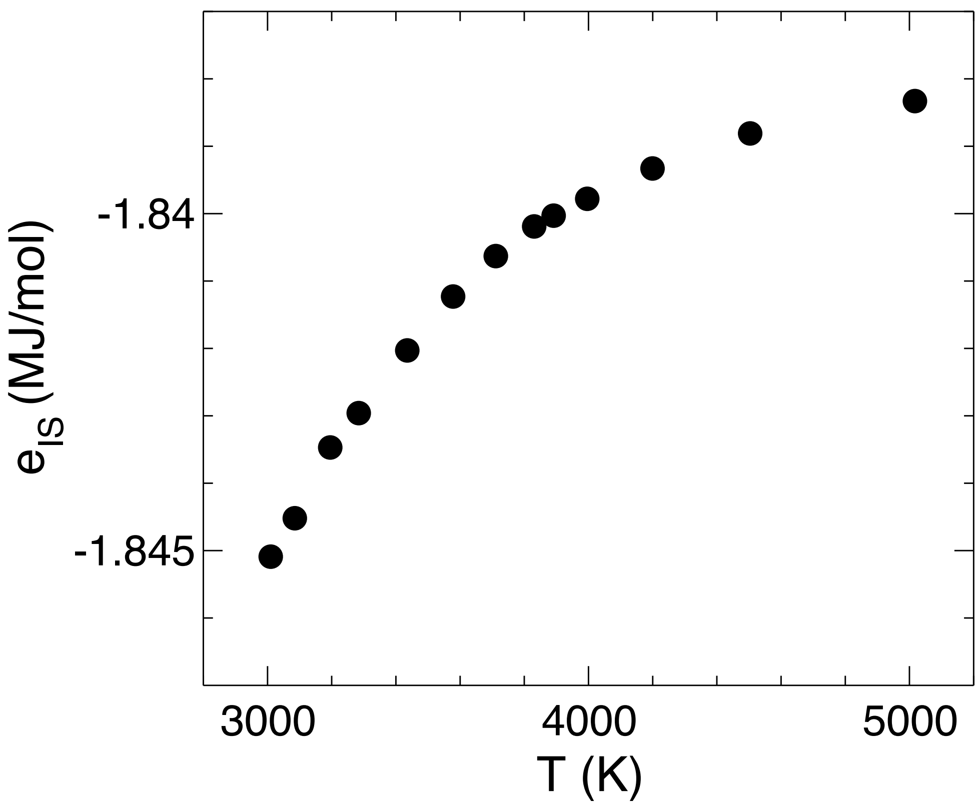
Phase Diagram:
Saika-Voivod, Sciortino, Grande, PHP, PRE 68, 011505 (2003)

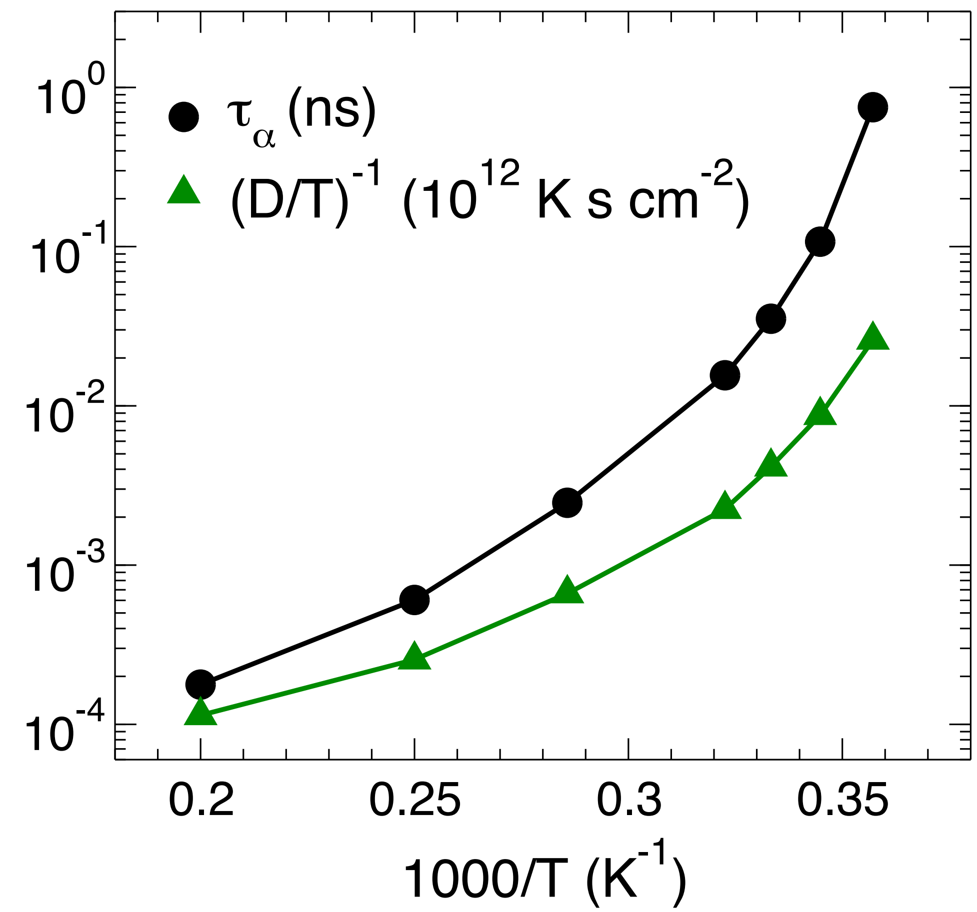
Crystal nucleation rates from CNT:
Saika-Voivod, PHP, Bowles, JCP 124, 224709 (2006)

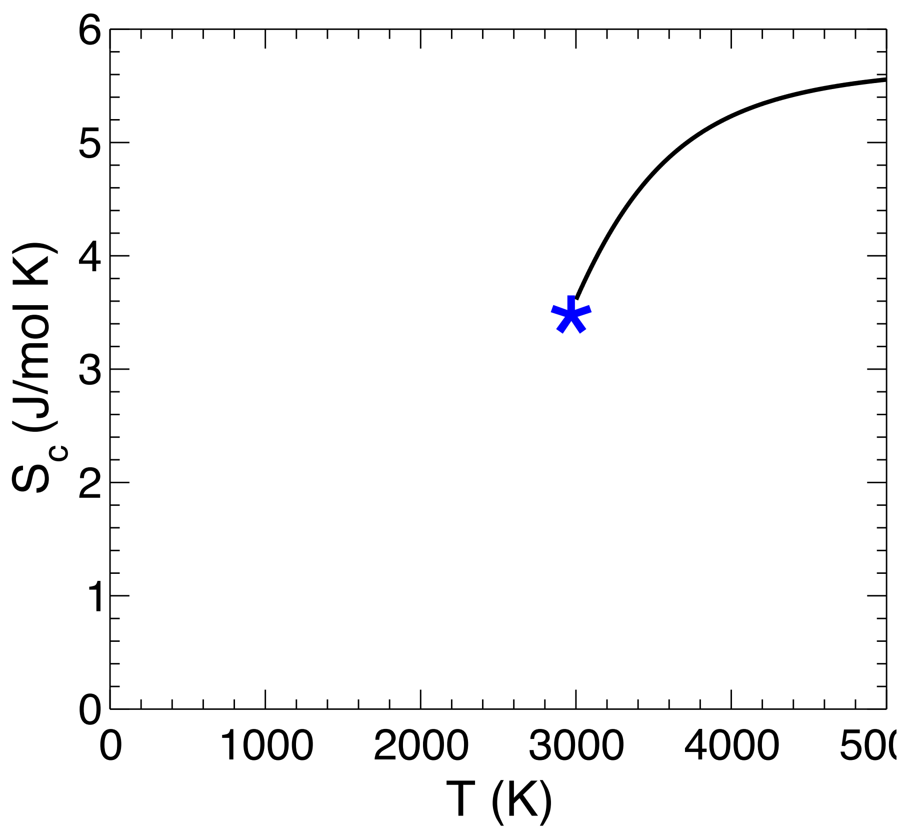
Intermediate scattering function of liquid silica at 3000K and 4.38 g/cm^3



Potential energy landscape, configurational entropy and fragile dynamics of liquid silica at 4.38 g/cm^3

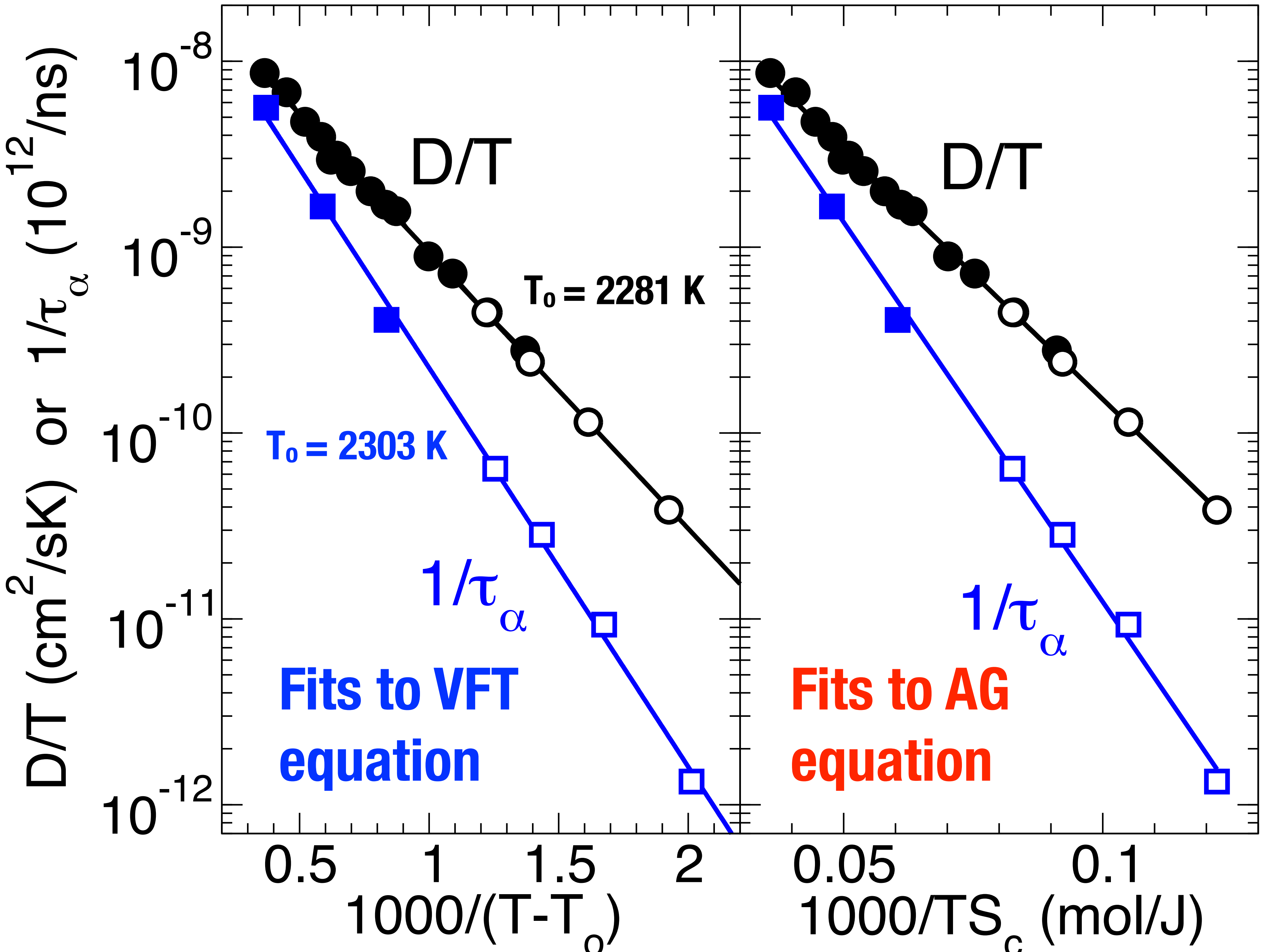






- For T<3100 K, τ_α and D evaluated from the longest un-nucleated runs
- τ_α found from fit of time dependence of the intermediate scattering function to stretched exponential, at q corresponding to the first peak of S(q).
- D found from mean square displacement vs time.

Modeling the dynamics of liquid silica at 4.38 g/cm^3



- Filled symbols: normal MD runs in which system does not crystallize
- Open symbols: data taken from longest un-nucleated run of crystallization study

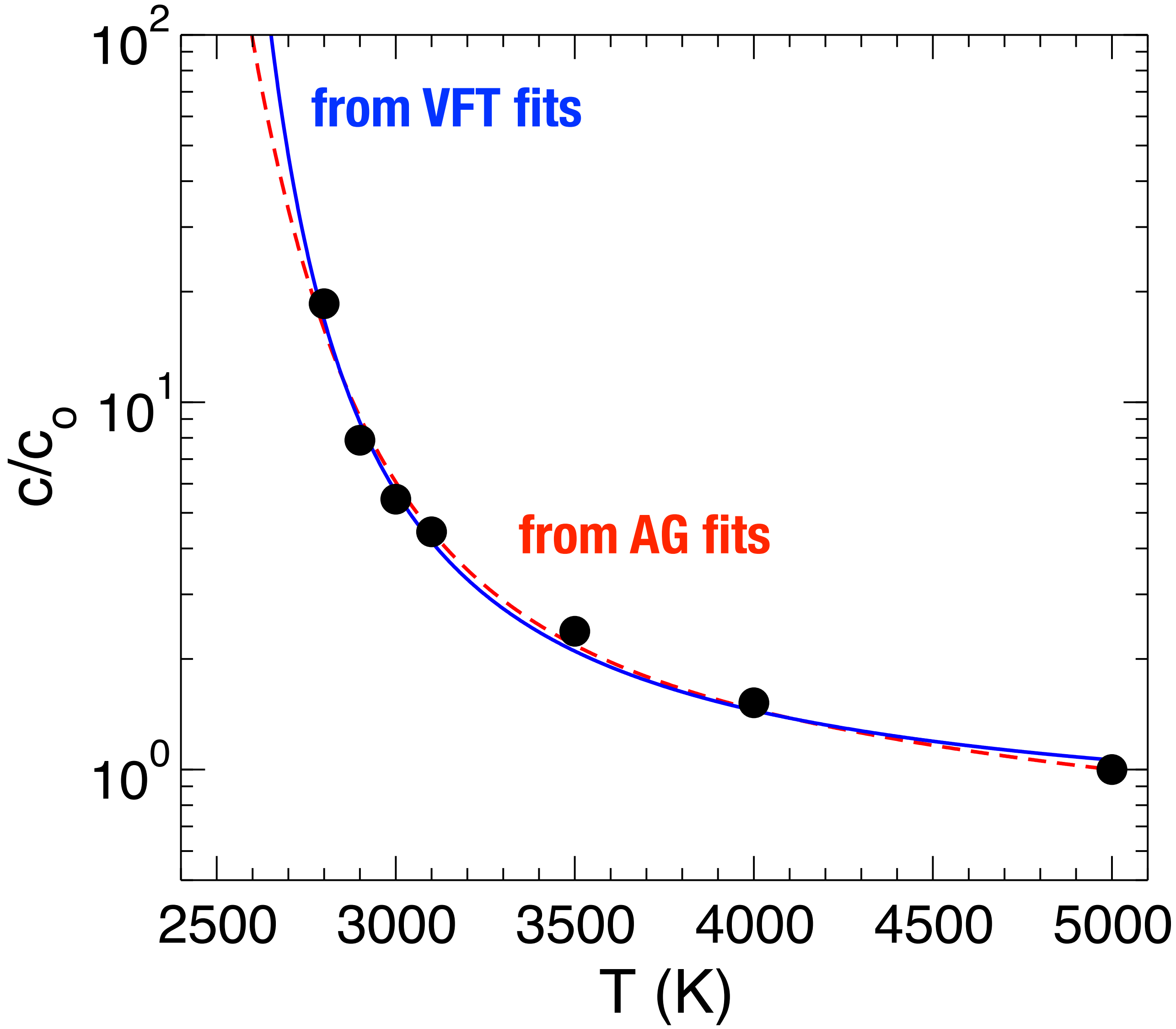
$$\frac{D}{T} = a\exp\left(\frac{b}{T-T_o}\right)$$

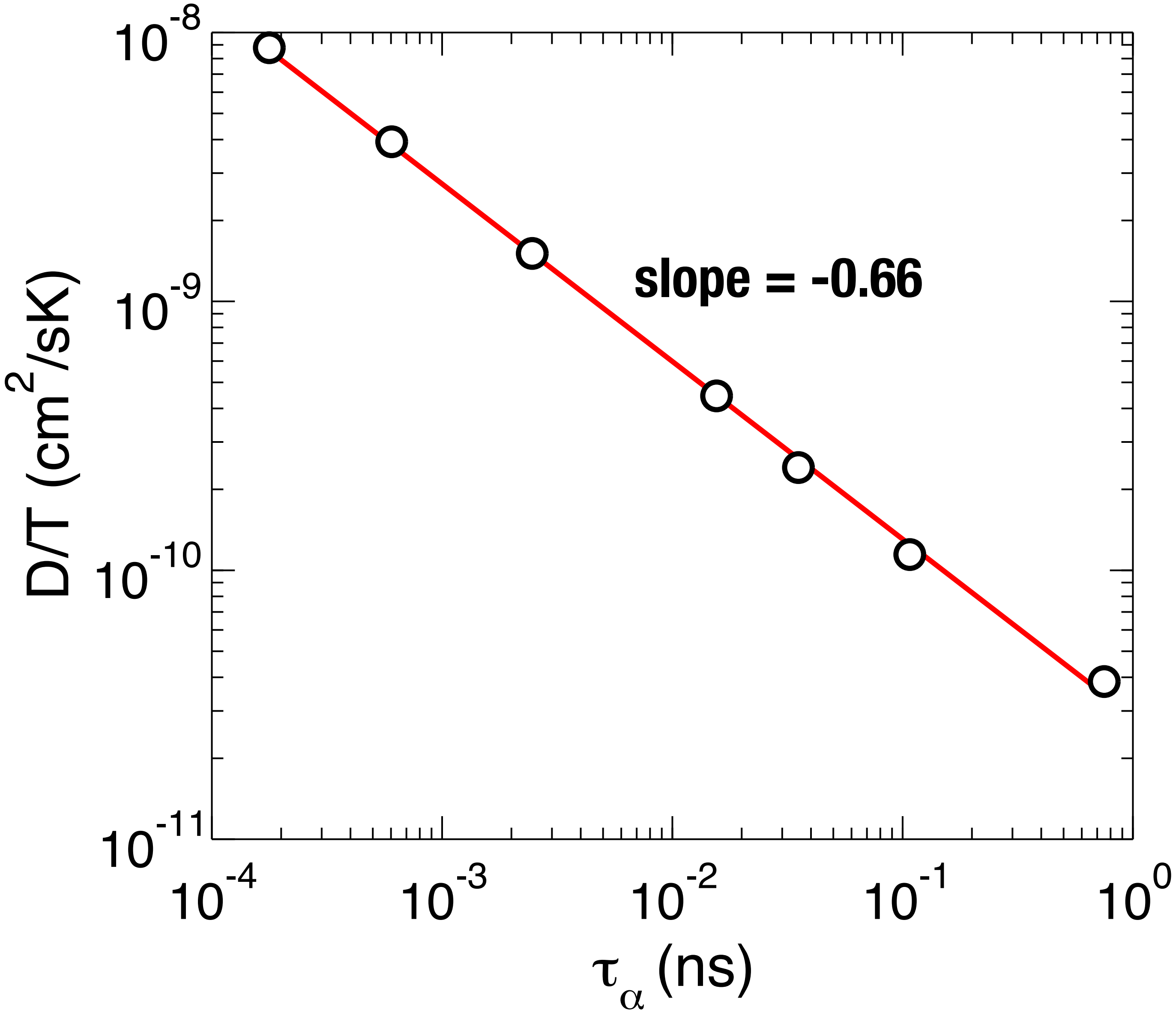
$$\tau_\alpha = c\exp\left(\frac{e}{T-T_o}\right)$$

$$\frac{D}{T} = A\exp\left(-\frac{B}{TS_c}\right)$$

$$\tau_\alpha = C\exp\left(\frac{E}{TS_c}\right)$$

Breakdown of the Stokes-Einstein relation in liquid silica at 4.38 g/cm^3





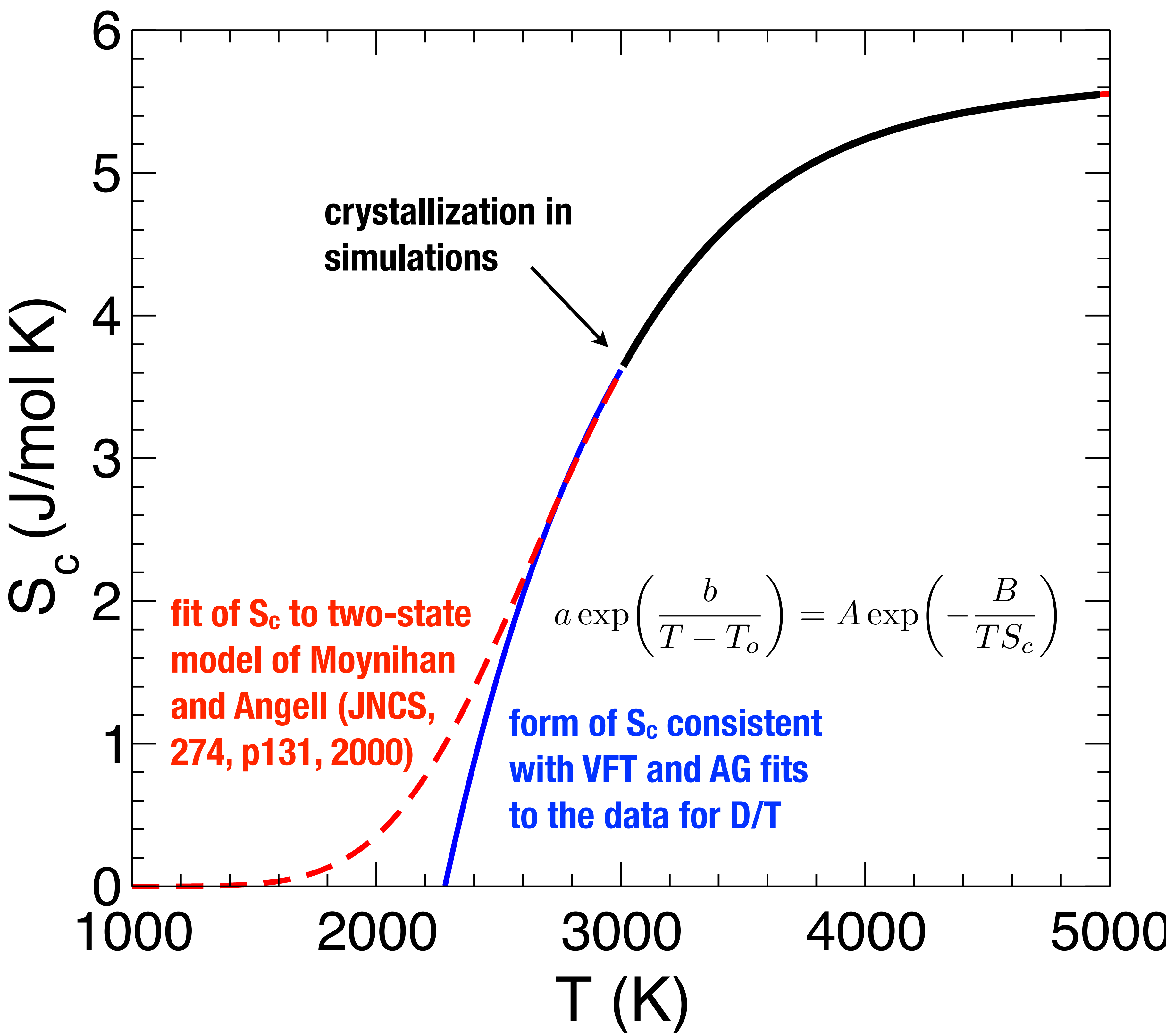
$$c = \frac{D\tau_\alpha}{T}$$

$$c_o = \lim_{T\to\infty} \frac{D\tau_\alpha}{T}$$

fractional Stokes-Einstein relation:

$$\frac{D}{T} \sim (\tau_\alpha)^{-\xi}, \quad \xi < 1$$

Low T extrapolation of the configurational entropy



Does crystallization impose a fundamental limit on studying the liquid at low T, or does it merely present a technical challenge?

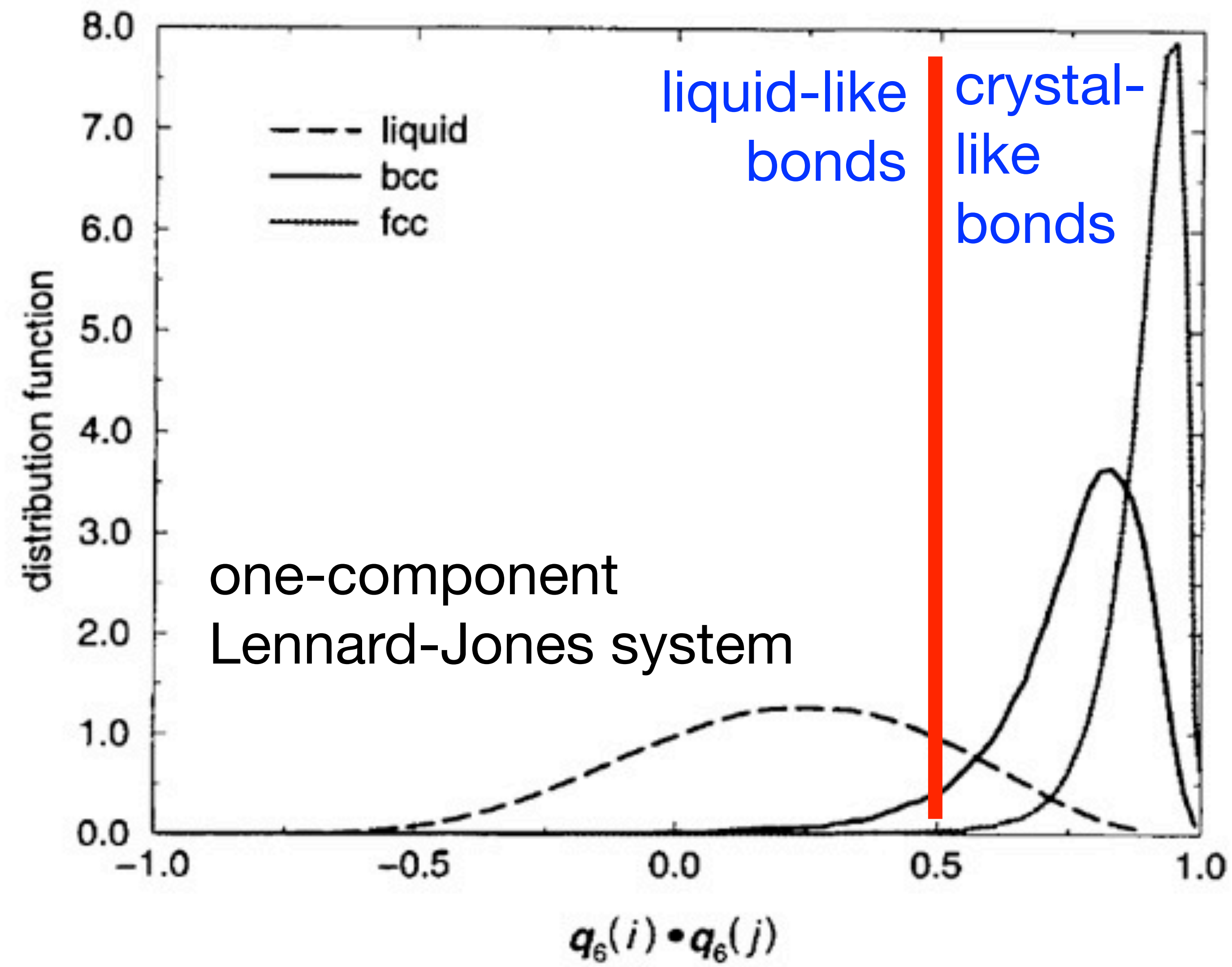
Identifying particles having crystal-like local environments

- We use the procedure developed by Frenkel and coworkers: defines a local orientational order parameter, based on spherical harmonics...
- See: Ten Wolde, Ruiz-Montero and Frenkel, JCP, 1996; Faraday Discuss., 1996.

$$\bar{q}_{lm}(i) \equiv \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{ij})$$

$$\tilde{q}_{6m}(i) \equiv \frac{\bar{q}_{6m}(i)}{\left[\sum_{m=-6}^{6} |\bar{q}_{6m}(i)|^2\right]^{1/2}}$$

$$\mathbf{q}_6(i) \cdot \mathbf{q}_6(j) \equiv \sum_{m=-6}^{6} \tilde{q}_{6m}(i) \tilde{q}_{6m}(j)^*$$



n_c = number of crystal-like bonds between a particle and its neighbors within the first coordination shell.

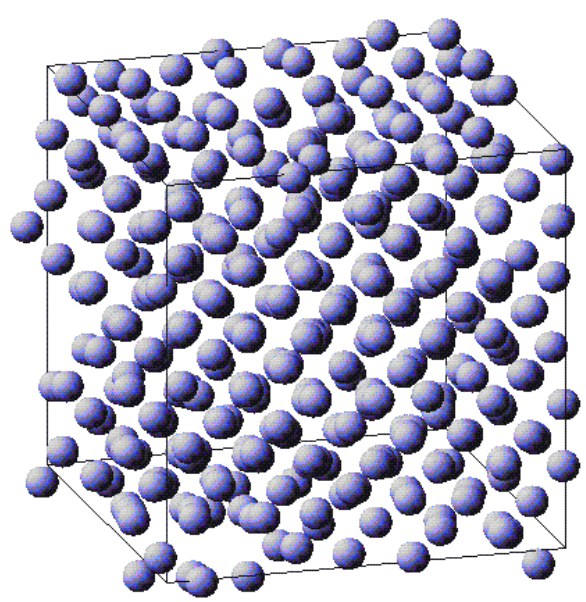
Identifying particles having crystal-like local environments

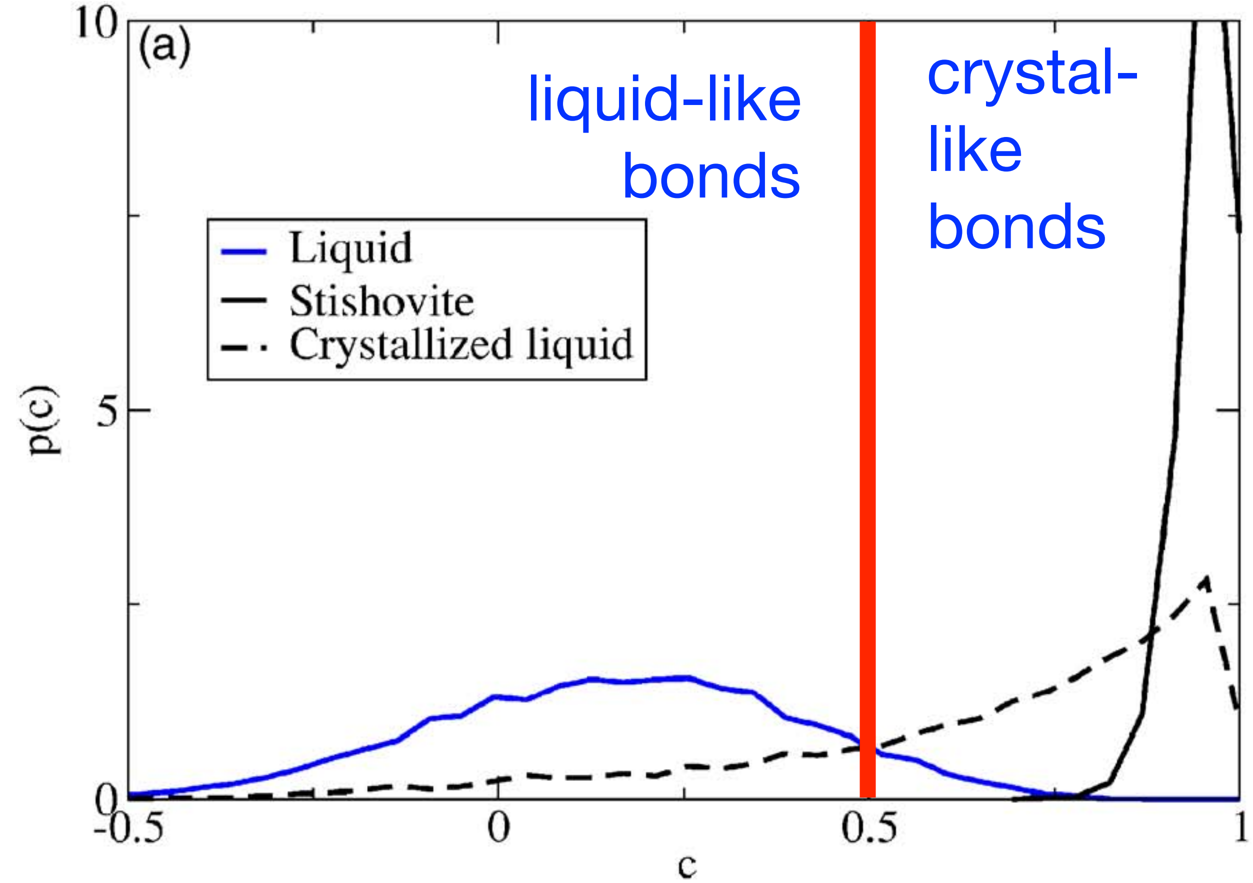
- We use q=8 instead of q=6, because q=6 does not select out cubic structures well. Stishovite is nearly cubic, and we do not want to assume the structure of the critical nucleus.

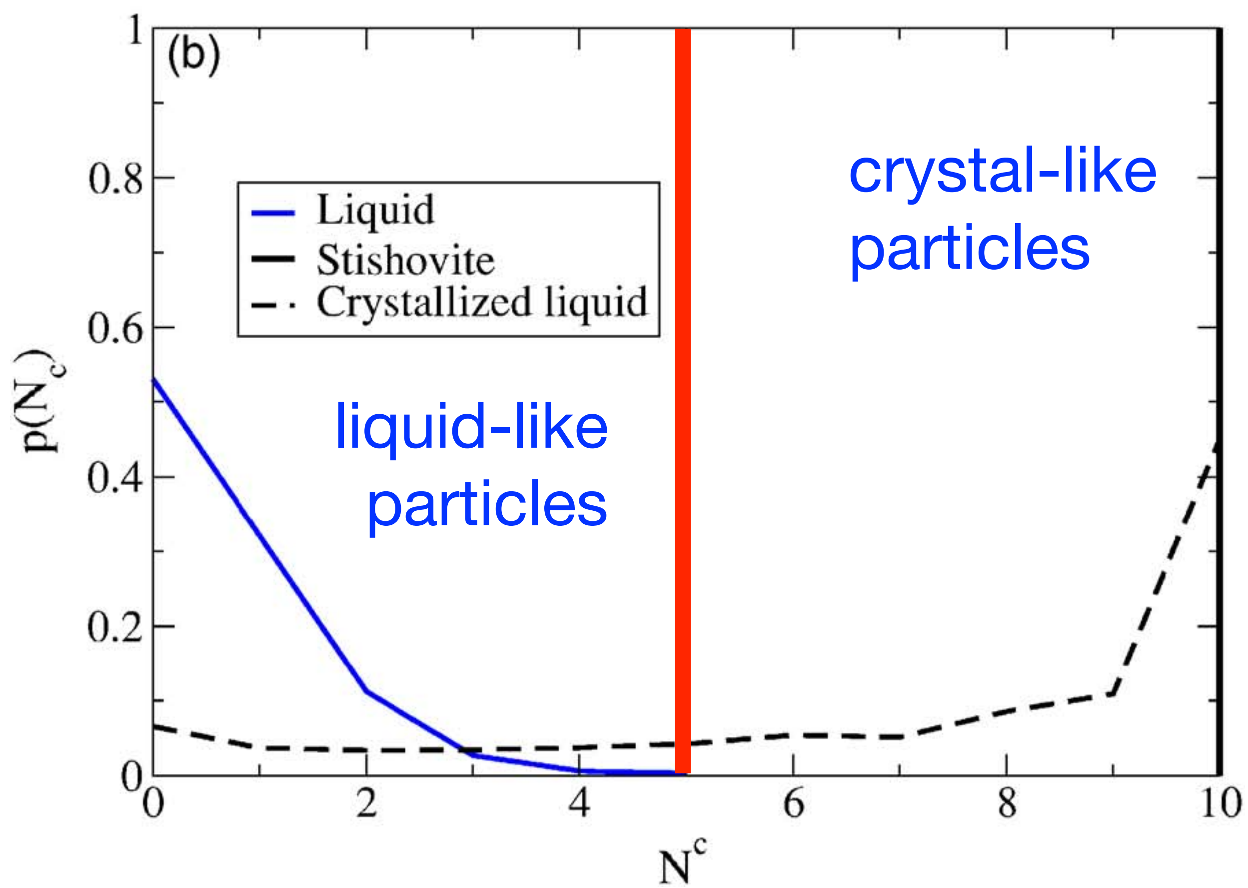
$$c_{ij} = \sum_{m=-8}^{8} \hat{q}_{8m}(i)\hat{q}^*_{8m}(j),$$

where

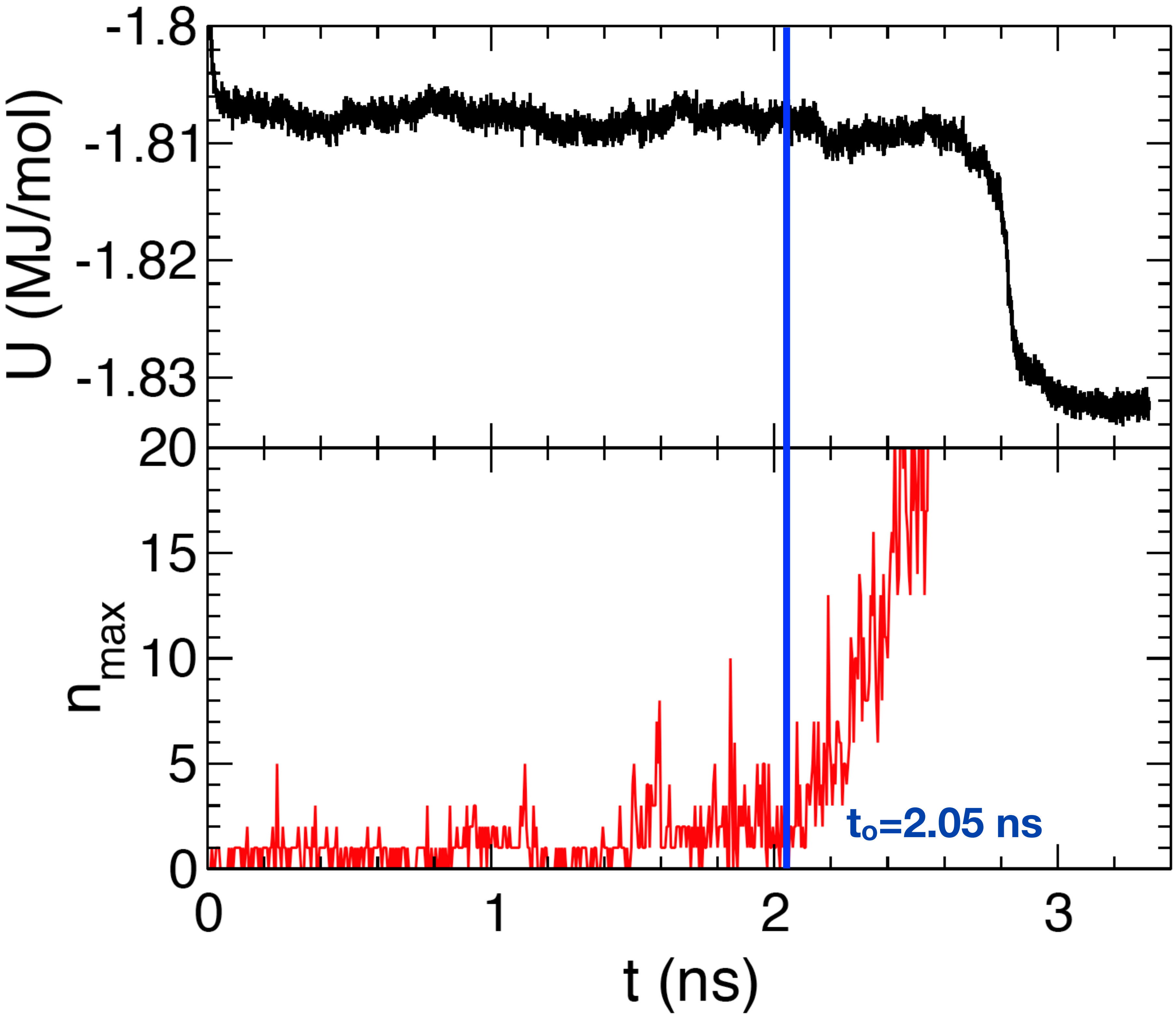
$$\hat{q}_{8m}(i) = \frac{q_{8m}(i)}{(\sum_{m=-8}^{8}|q_{8m}(i)|^2)^{1/2}}$$





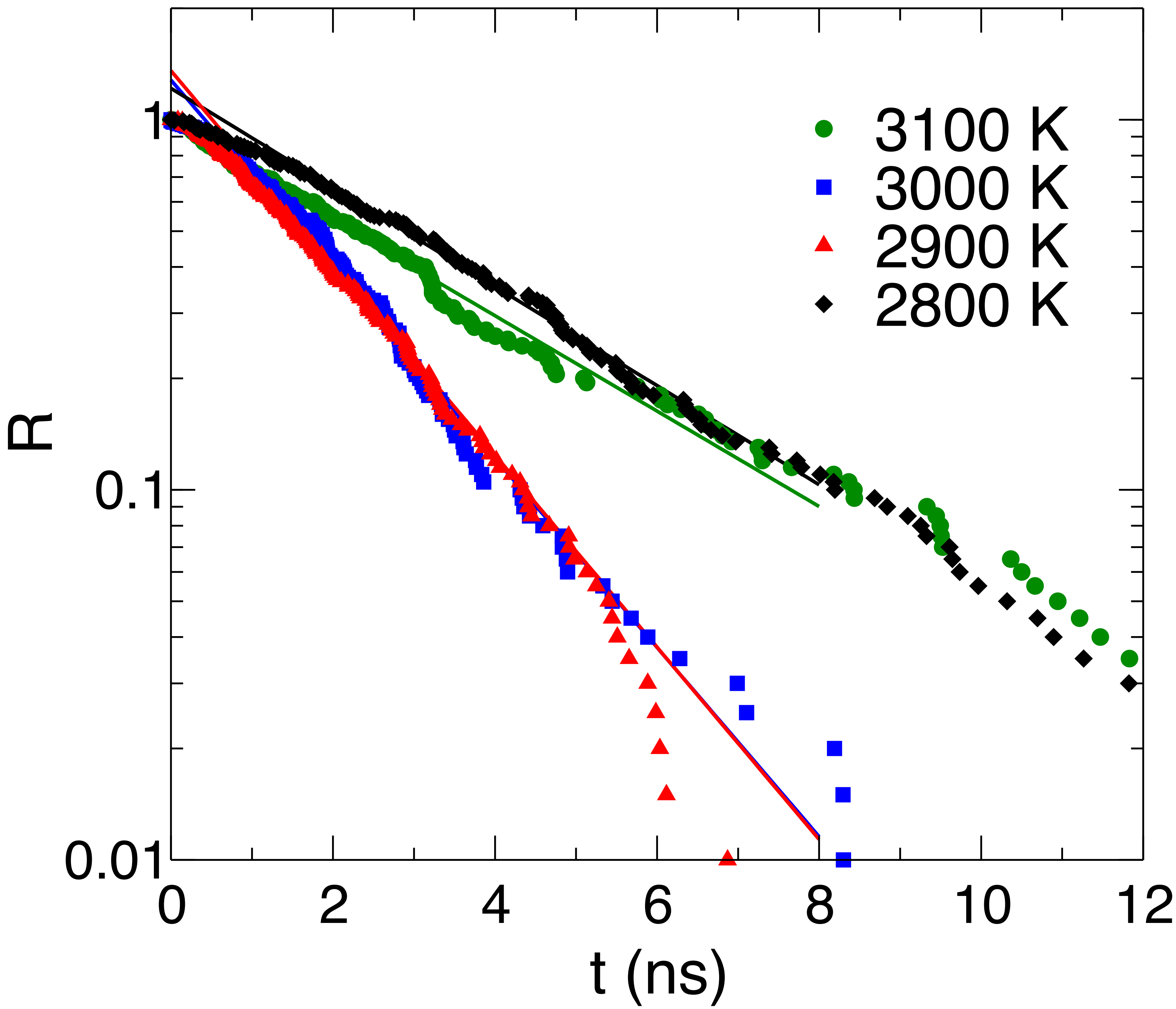


Measuring the nucleation time: a single MD run at 2900 K, starting from 5000 K



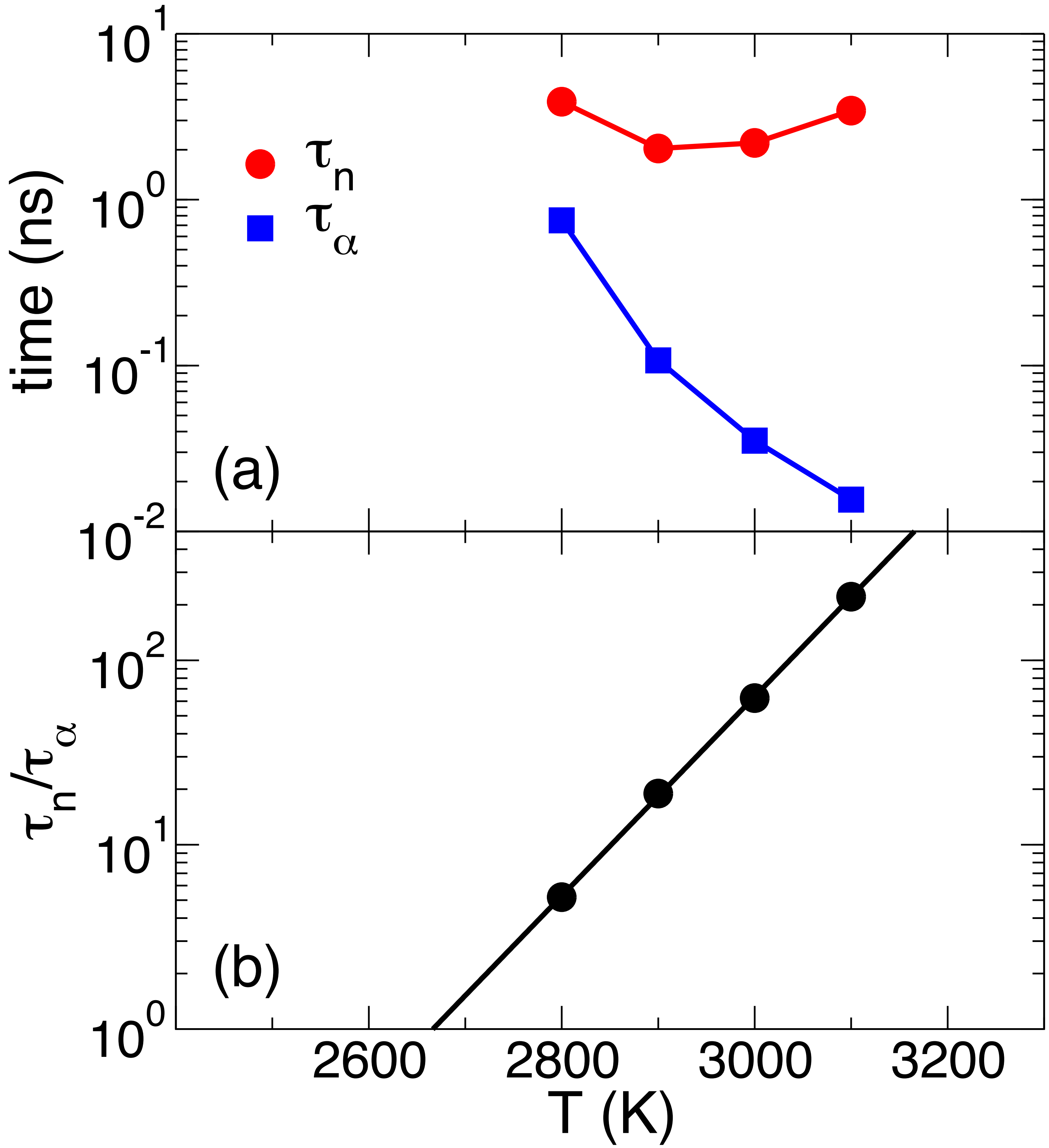
- evolution of the potential energy U as a function of time following a temperature jump from 5000 K
- n_{max}, size of the largest crystalline cluster, as a function of time
- nucleation time t_o in an individual run is defined as the last time that n_{max}=0.

Evaluating the mean nucleation time



- 200 runs at each T
- R is the number of runs remaining un-nucleated after time t.
- slope gives system nucleation rate (JV)
- characteristic nucleation time $\tau_R = (JV)^{-1}$
- We also evaluate the mean nucleation time $\tau_o = \langle t_o \rangle$

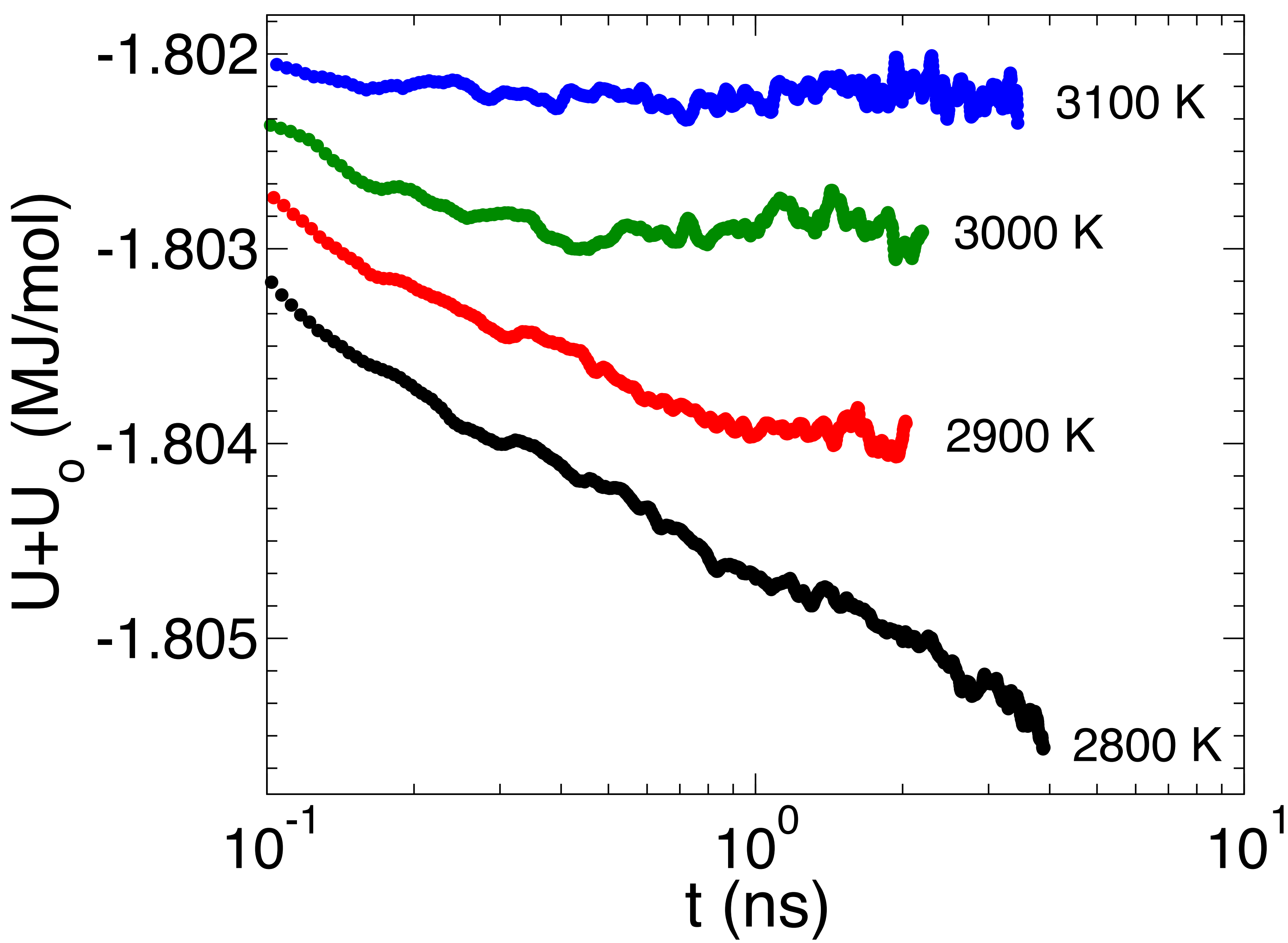
Crystal nucleation time compared to alpha relaxation time



τ_n = mean nucleation time, i.e. average of latest time that the max cluster size was zero, over all 200 runs at each T

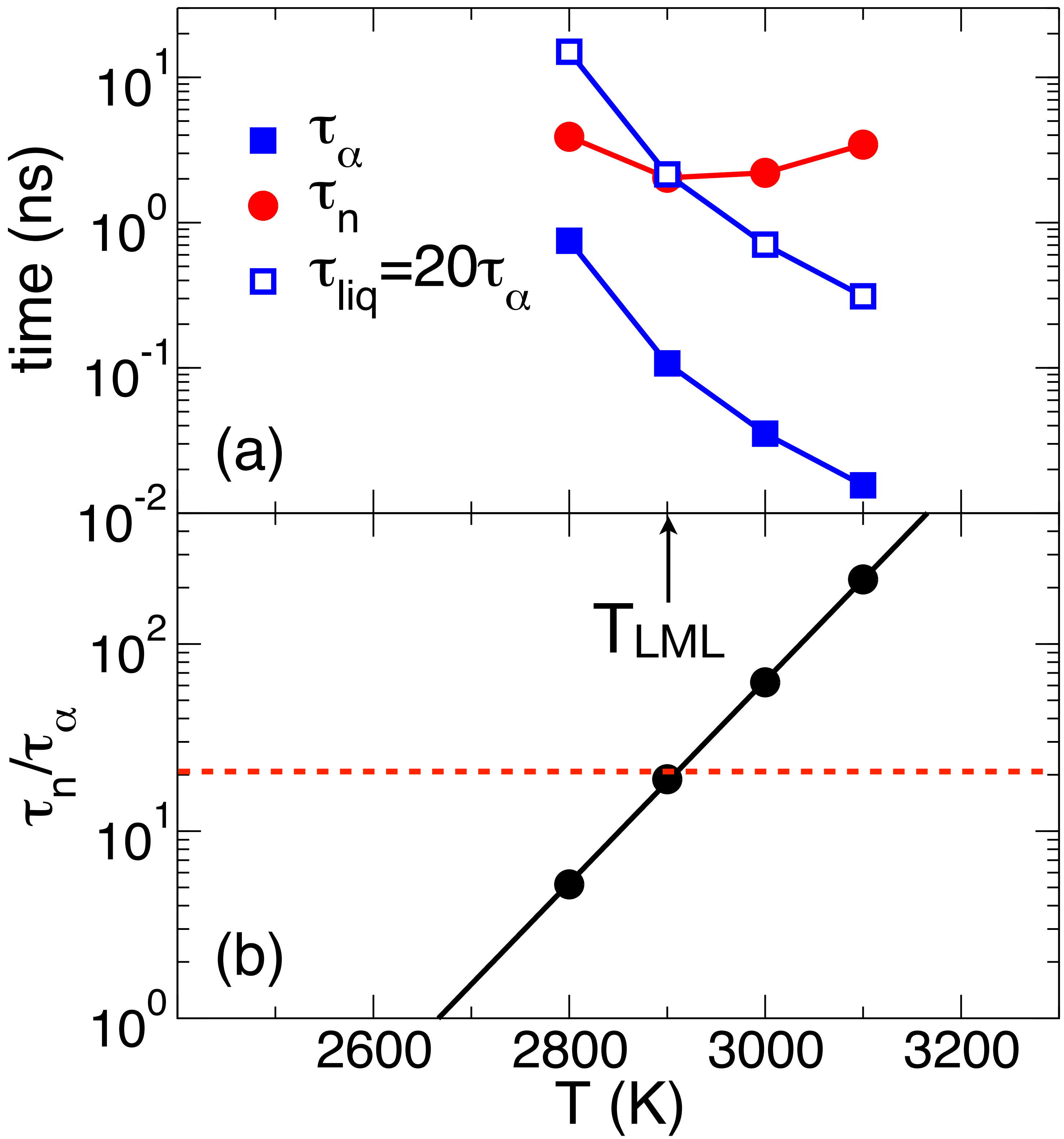
System is approaching a kinetic limit, below which crystallization will occur faster than equilibration.

Crossover from steady-state to transient nucleation



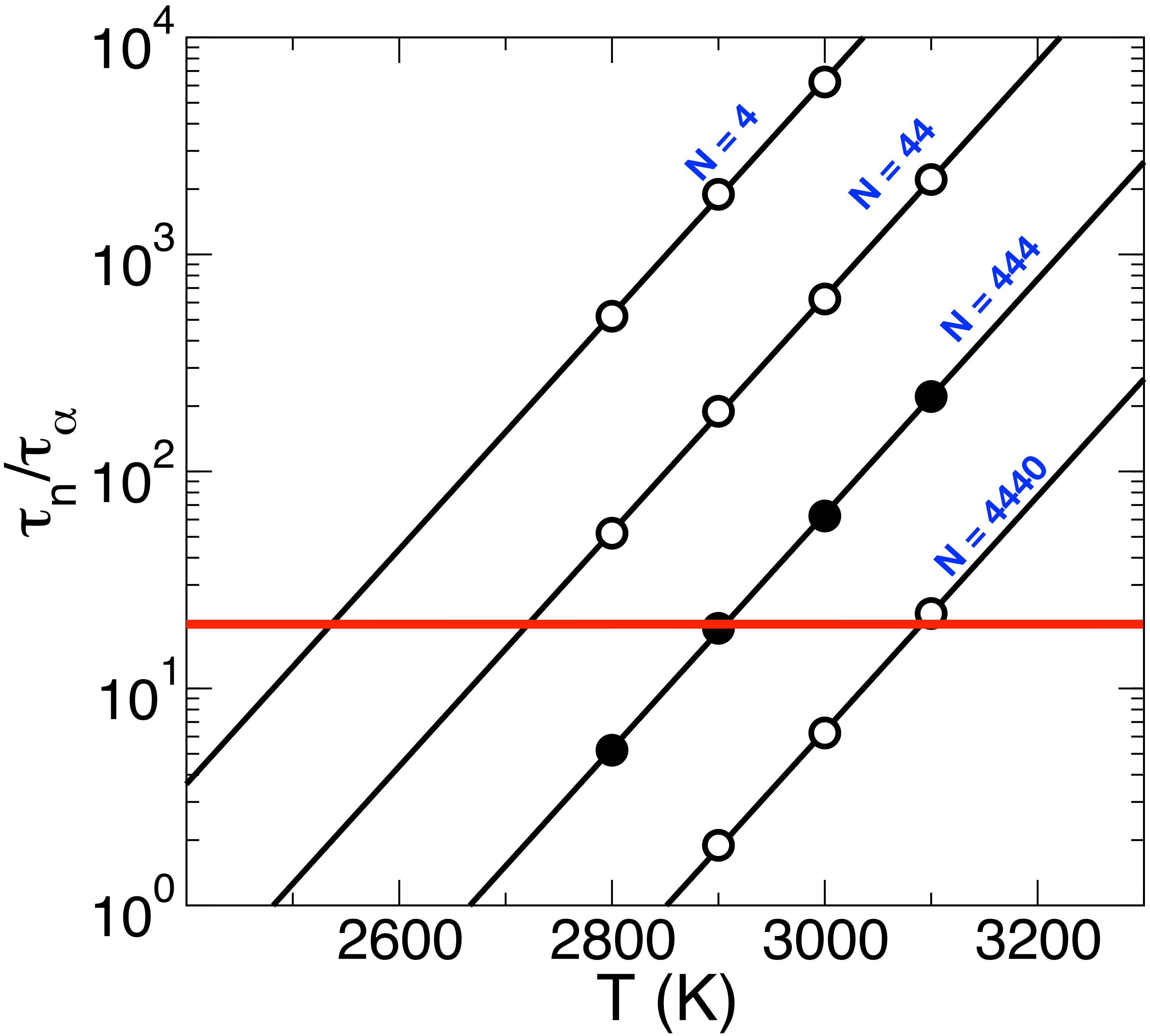
- 200 quenches from 5000 K to each T.
- U = system potential energy, averaged over all runs that remain un-nucleated at that t.
- Each curve ends at $t=\tau_n$ for that T.
- Indicates that below 2900 K, the crystal typically nucleates before the liquid can equilibrate

Shifting τ_α to model the crossing of the nucleation and equilibration times



- Data for U indicate that the crossover from steady-state to transient nucleation occurs at about 2900 K.
- We model the system equilibration time τ_{liq} by taking a multiple of τ_α such that the curves cross at 2900 K.

Influence of system size on nucleation time



$$\tau_{\rm n} = (JV)^{-1}$$

- τ_n is the nucleation time for the *system*.
- Larger system will nucleate quicker, smaller system will take longer.
- But even the smallest credible system size nucleates on the time scale of equilibration at finite T (approx 2700 K)...
- ...i.e. we cannot avoid crystallization by using smaller systems.

If SE breakdown did not occur, what would the nucleation time be?

CNT nucleation time is

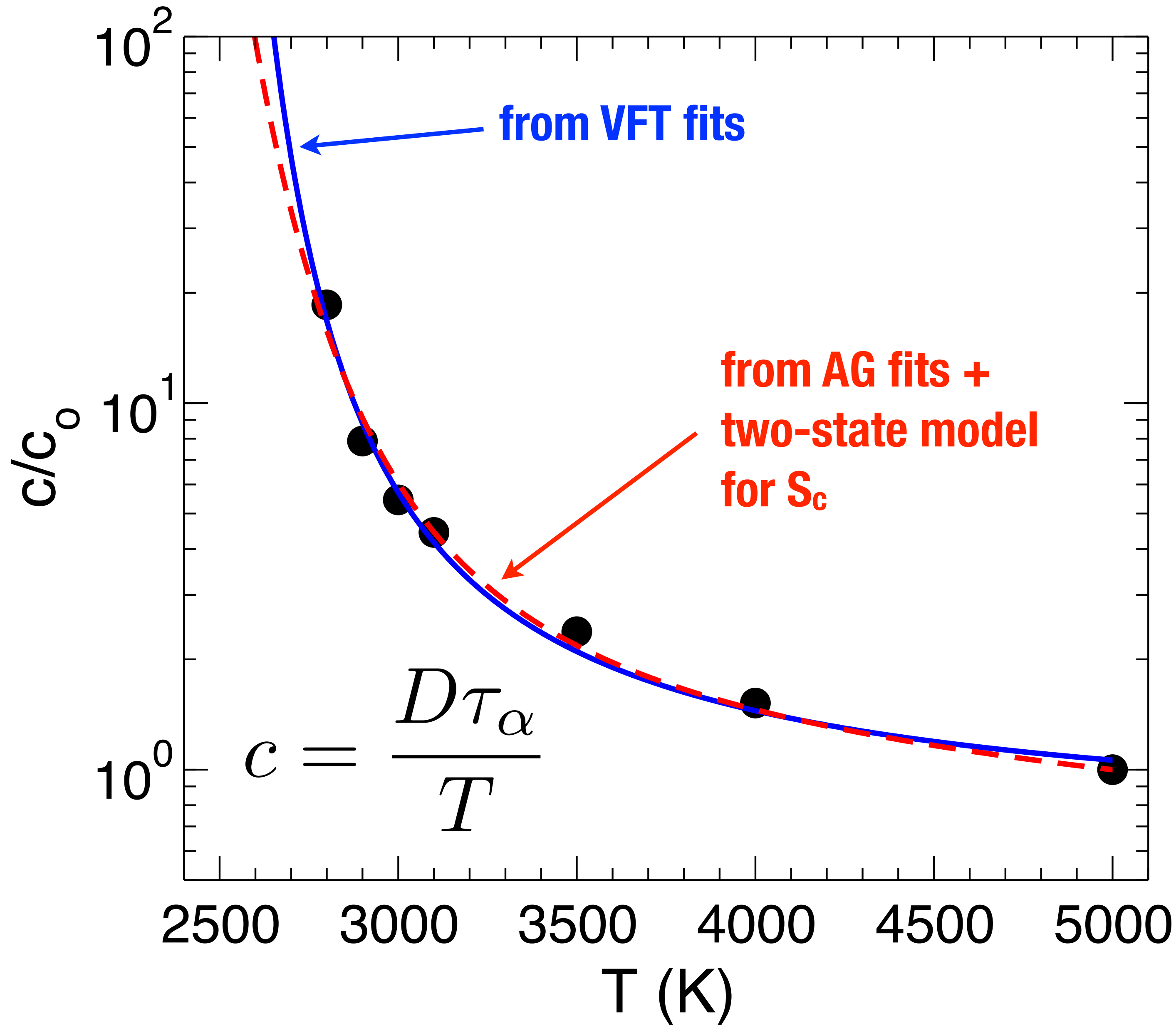
$$\tau_{\rm n} = A\, D^{-1} \exp\left(\frac{\Delta G(n^*)}{kT}\right).$$

Let $D_{\rm SE}$ be the value D would have if SE breakdown did not occur. This can be found from,

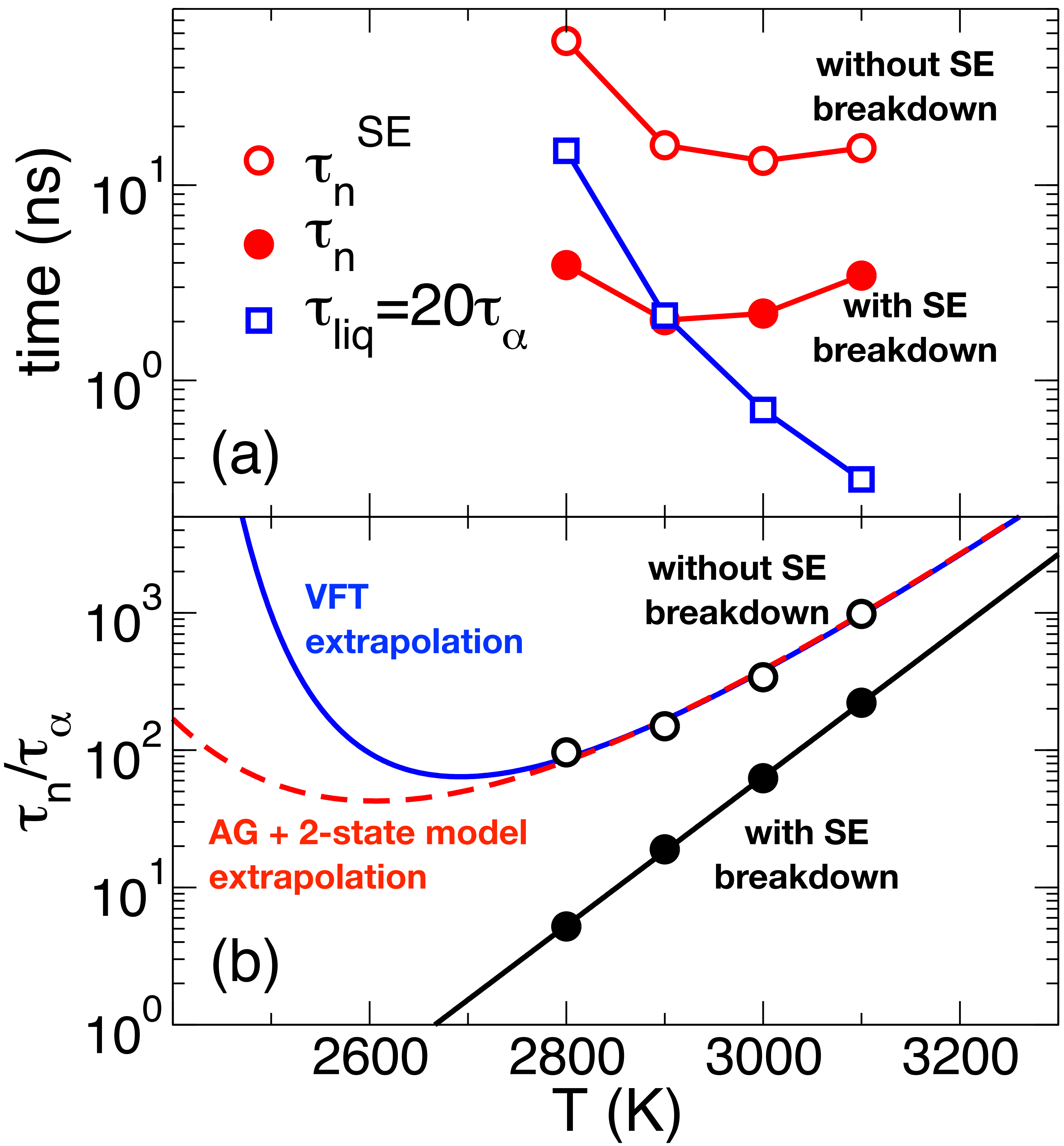
$$D_{\rm SE} = \frac{c_o T}{\tau_\alpha}.$$

We can then find $\tau_{\rm n}^{\rm SE}$, the value $\tau_{\rm n}$ would have in the absence of SE breakdown,

$$\tau_{\rm n}^{\rm SE} = \left(\frac{D}{D_{\rm SE}}\right)\tau_{\rm n} = \left(\frac{c}{c_o}\right)\tau_{\rm n}.$$

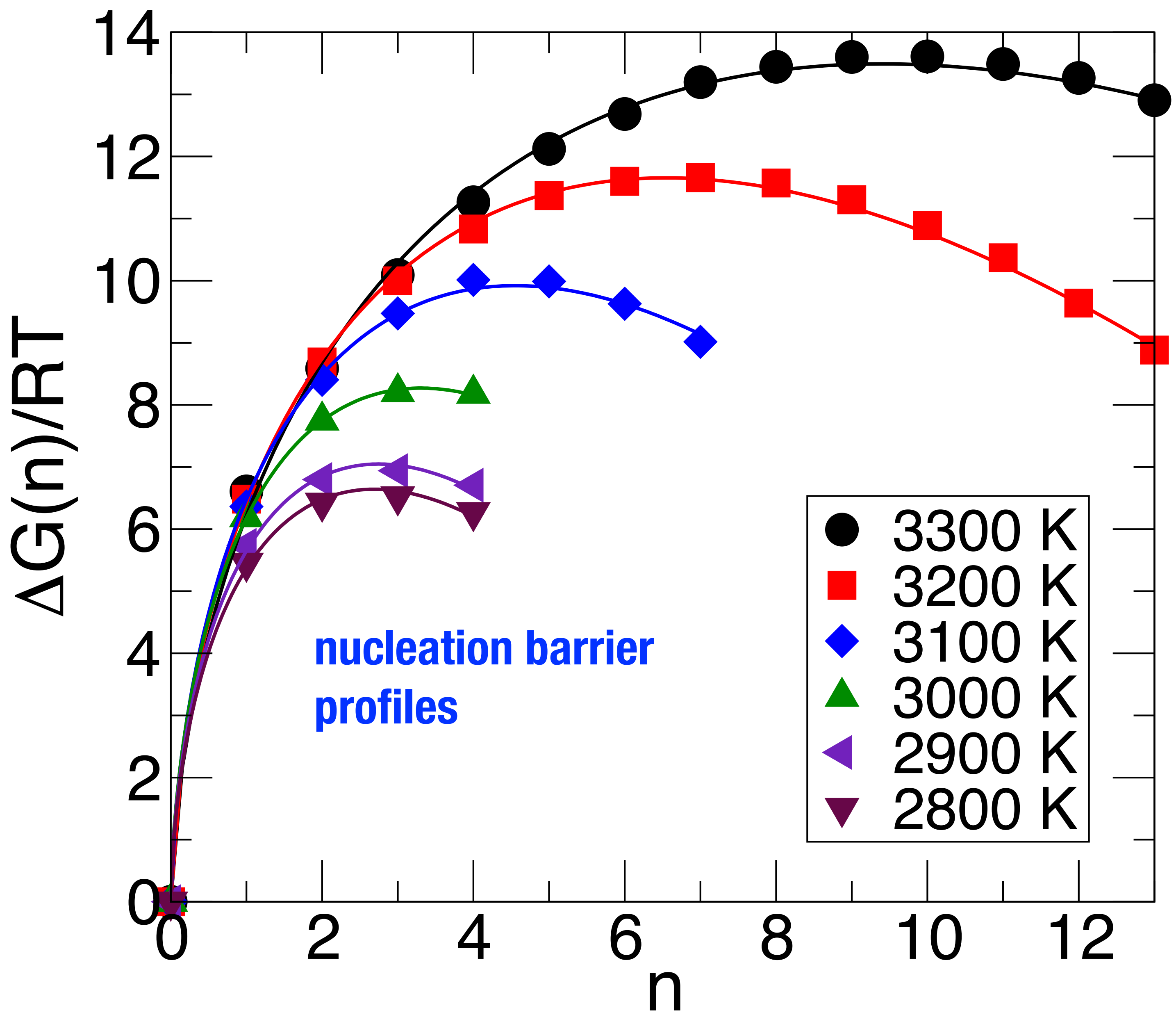


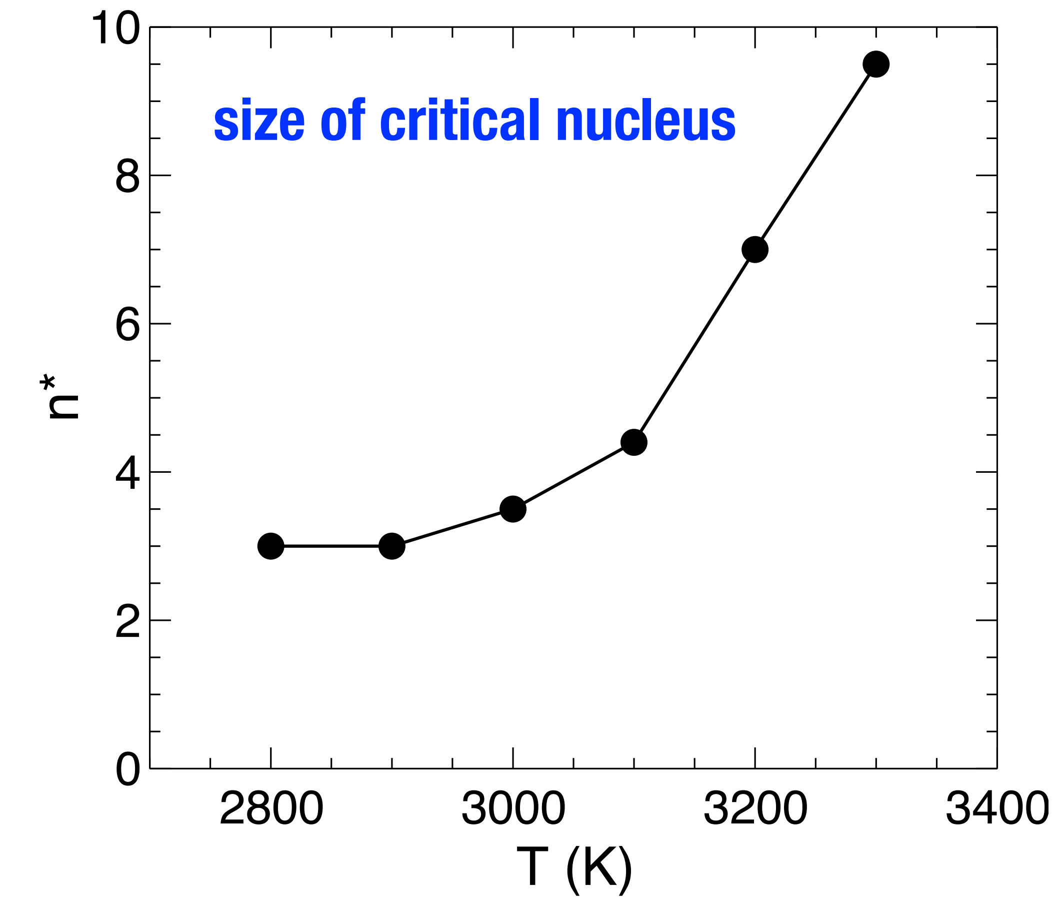
Nucleation time vs T with and without SE breakdown

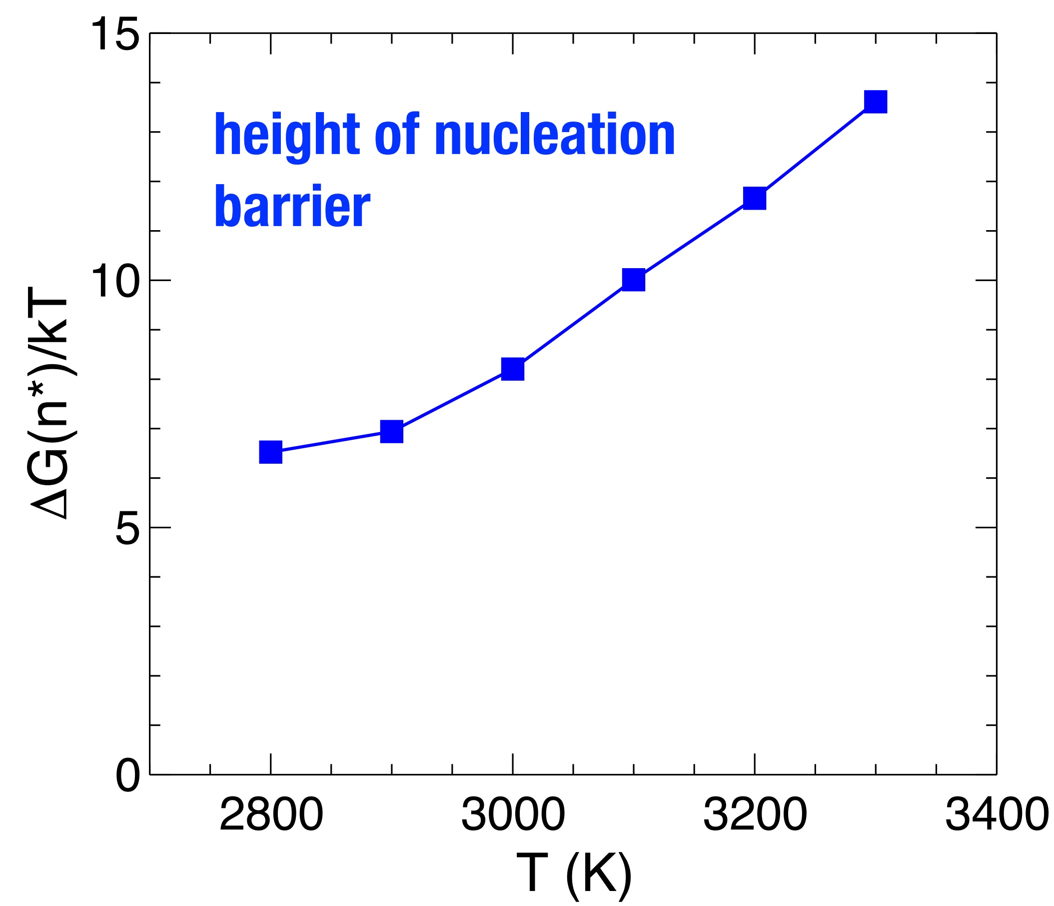


- SE breakdown in this system is sufficiently strong to account for the onset of transient nucleation.
- Consistent with Tanaka's proposal that the presence of T_{LML} is induced by SE breakdown
- Does not mean that other mechanisms do not contribute.
- Entropy catastrophe would be accessible, were it not for SE breakdown.

Nucleation barrier and size of critical nucleus







- The size of the critical nucleus becomes small...
- ...and the height of the nucleation barrier is dropping...
- ...but neither go to zero. The liquid maintains a (weak) thermodynamic stability against crystallization...i.e. there is no crystal “spinodal”.

Can we find $\Delta G_{liq}(T)$...to compare to $\Delta G_{nuc}(T)$?

- Adam and Gibbs (JCP, 1965) describe the average transition probabilities for cooperative rearrangements in a supercooled liquid as...

$$\bar{W}(T) = A \exp\left(-\frac{\Delta G_{\rm liq}}{kT}\right) = A \exp\left(-\frac{C}{TS_c}\right)$$

- ...where ΔG_{liq} is the free energy difference between a subsystem that is "rearrangeable", and the system free energy. That is, it is the work required to form a cooperatively rearranging region.

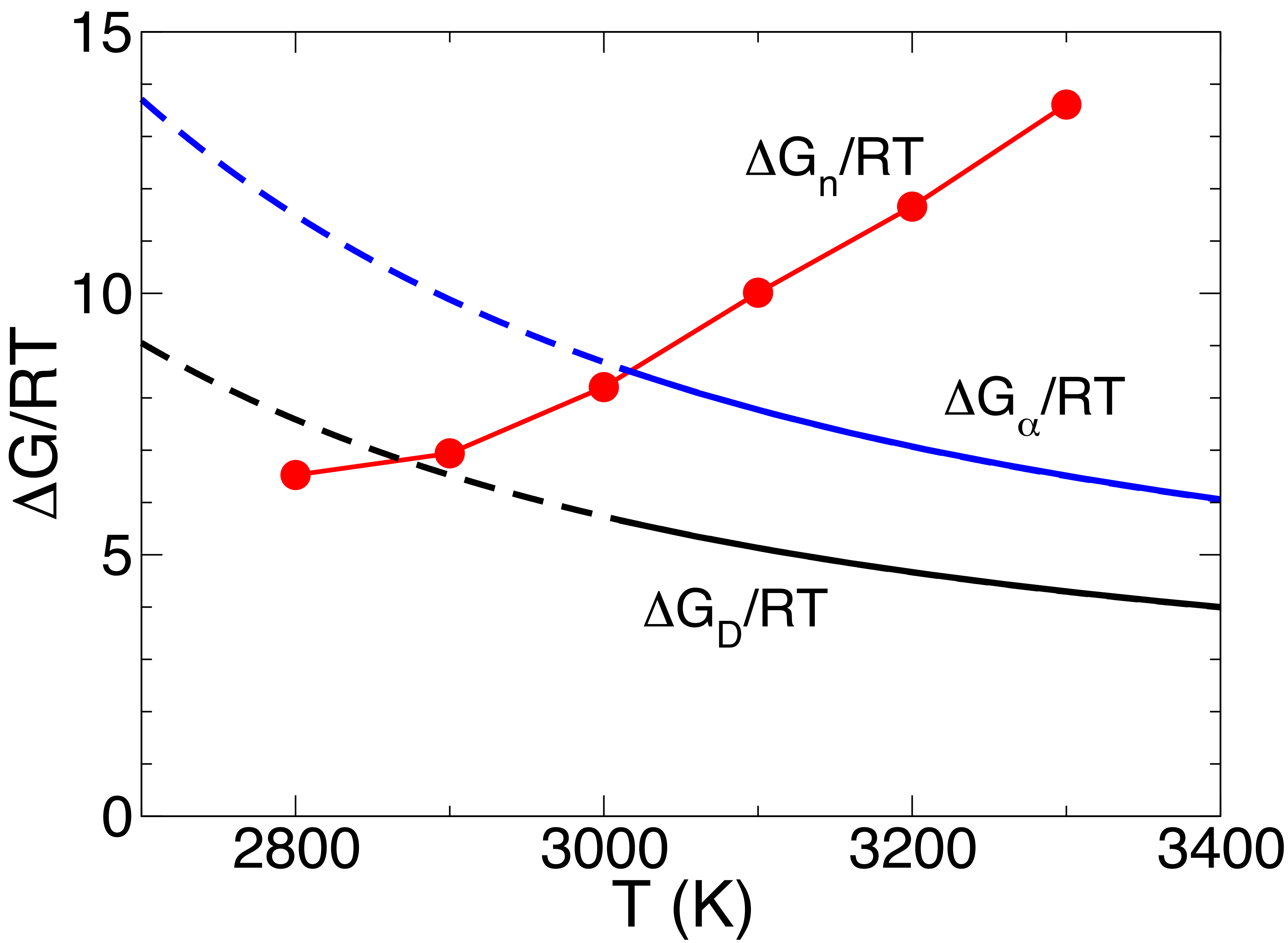
- Since the alpha relaxation time satisfies the AG relation in the form of...

$$\tau_\alpha = K \exp\left(\frac{C_\alpha}{TS_c}\right)$$

- ...then ΔG_{liq} as defined in the AG theory can be estimated from...

$$\frac{\Delta G_{\rm liq}(T)}{kT} \simeq \frac{\Delta G_\alpha(T)}{kT} = \frac{C_\alpha}{T\,S_c(T)}$$

Free energy barriers to crystal nucleation and liquid-state relaxation in BKS silica



- Can the kinetically-defined crystallization limit be expressed in terms of thermodynamic barriers, to realize Kauzmann's idea? Perhaps...
- In the T range of the kinetic limit, the molecular rearrangements required to remain a liquid (i.e. alpha relaxation) and those required to leave the liquid state (via nucleation) occur on similar free-energy scales.
- Caution: Equal barriers do not correspond to equal times.

Conclusions

- BKS silica at this density seems to exhibit an unavoidable, finite-T, kinetically-defined limit on the liquid state, due to crystallization (...consistent with Kauzmann's 1948 idea).

- The presence or absence of glassy dynamics in the liquid (i.e. SE breakdown) is crucial for the existence of this limit (...as Tanaka predicted).

- Next steps:
  - Does this kinetic limit correspond to a thermodynamic limit?
  - Examine role of dynamical heterogeneities, and their relationship to pre-critical crystal embryos.