Localized Excitations, Facilitation and Non-equilibrium Broken Symmetry

David Chandler

with

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and

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Rob Jack (Berkeley/Bath), **Aaron Keys** (Michigan),

Excitations

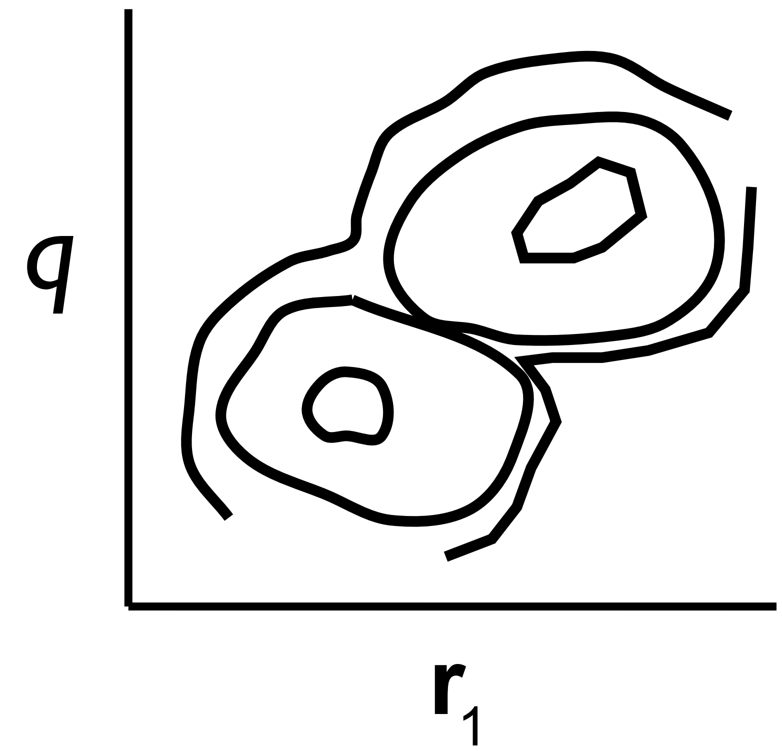
Sample $P\left[x(t)\right]C_{\text{excitation}}\left[x(t)\right]$

$C_{\text{excitation}}\left[x(t)\right] = 1,$ if at least once in trajectory of length Δt

$\Delta r(t) = |\mathbf{r}_1^{(\text{quenched})}(t) - \mathbf{r}_1^{(\text{quenched})}(0)| > \sigma$

AND $\Delta r(t + \Delta t) > \sigma,$

$= 0,$ else.



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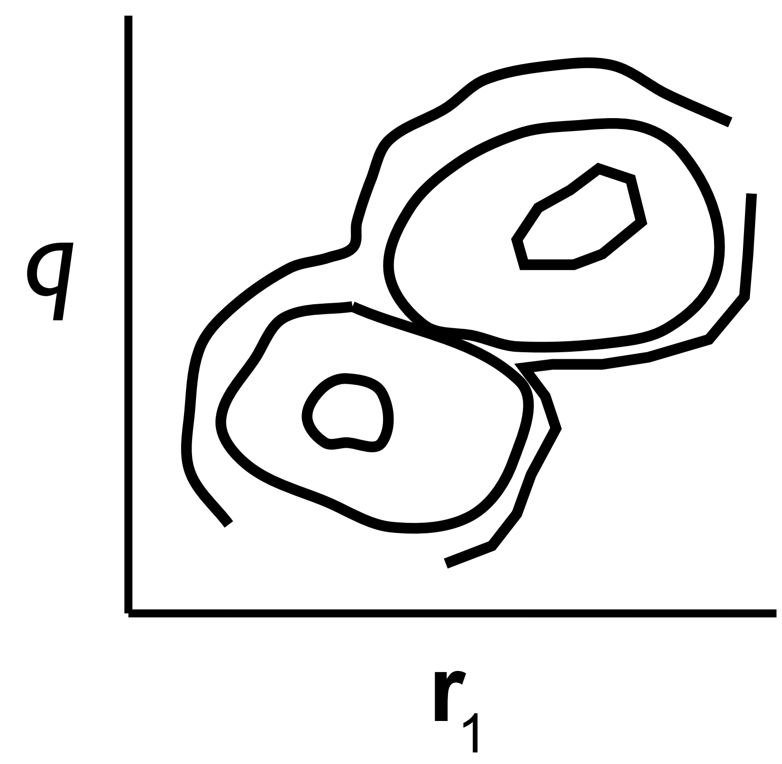

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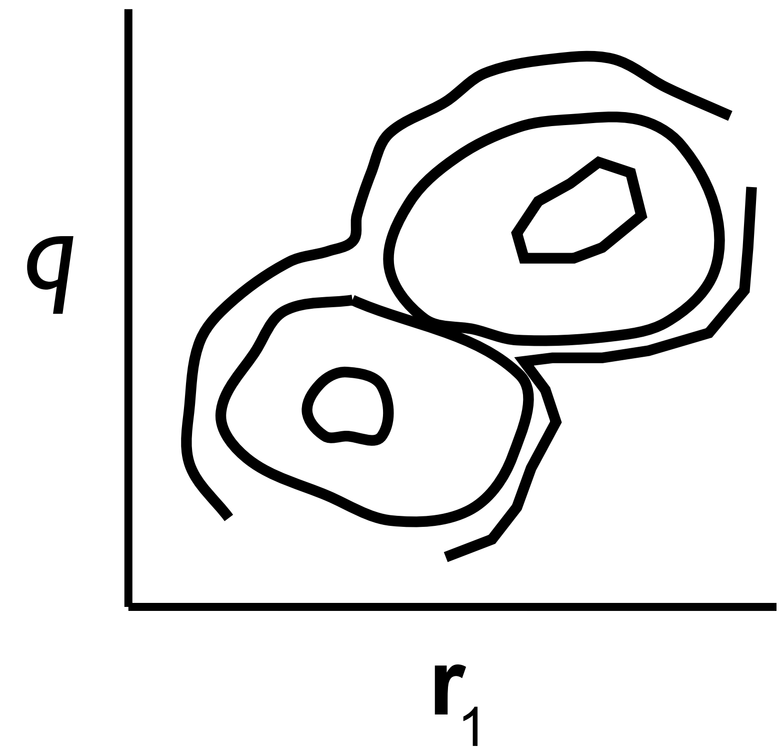

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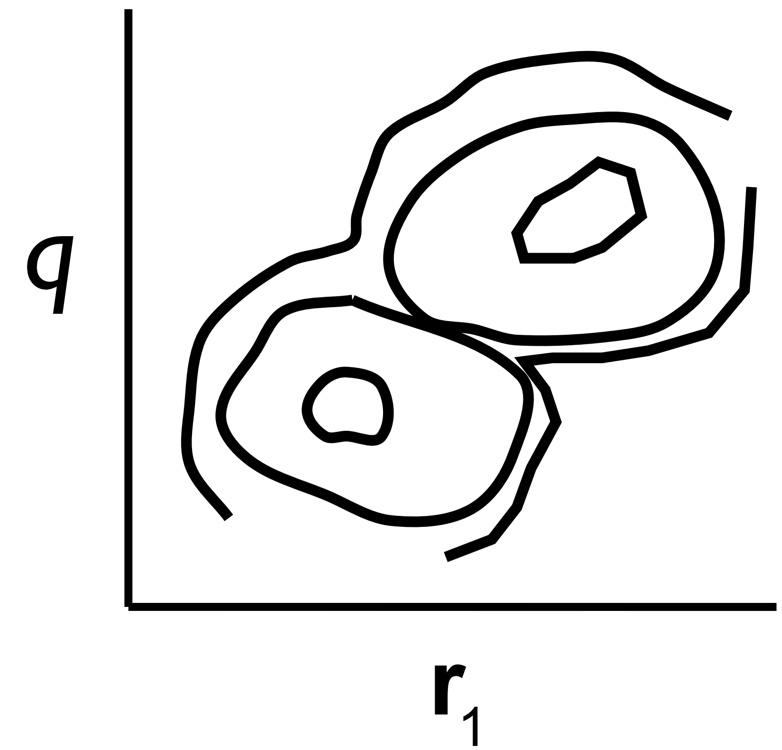

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δt = coarse graining time $<$ Δt = time to detect excitation

$\Delta t \ll \tau$ = structural relaxation time

Excitations (mobility) atoms packed & disordered

d=2 WCA mixture, T_o=1.5 Blue, $\Delta r_i(t) = |\mathbf{r}_i^{(\text{coarse})}(t) - \mathbf{r}_i^{(\text{coarse})}(0)|=0$; red, $\Delta r_i(t) \geq \sigma$

T=0.1

T=0.5

T=1.0

Keys, Hedges, Chandler & Glotzer, in preparation (2010)

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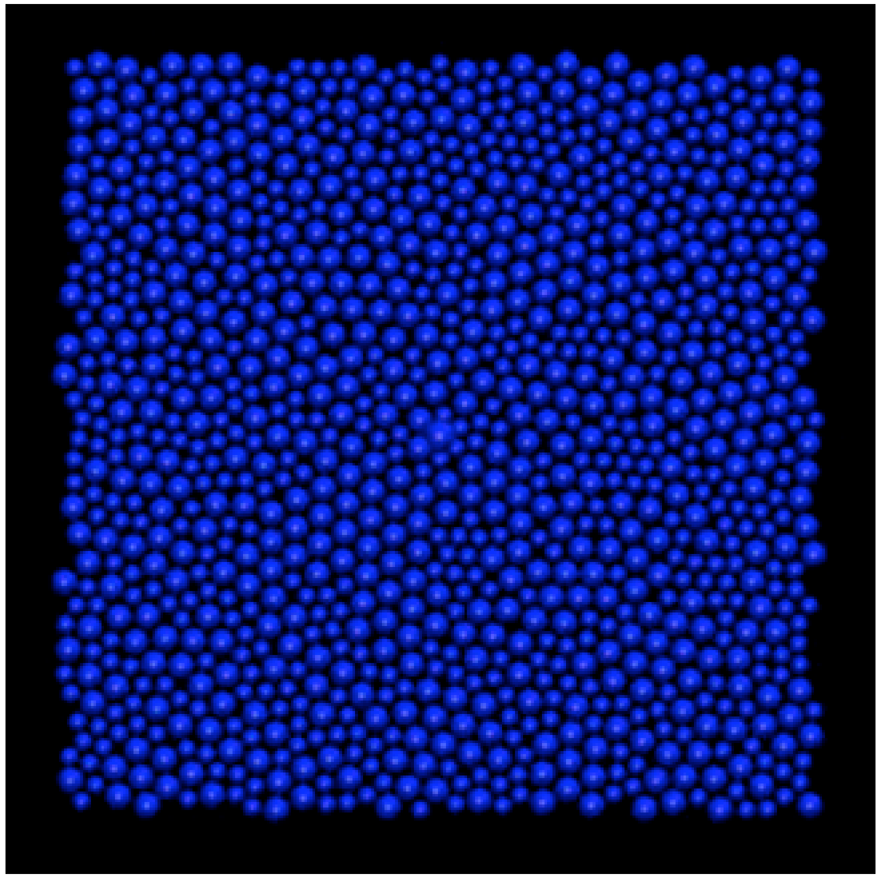

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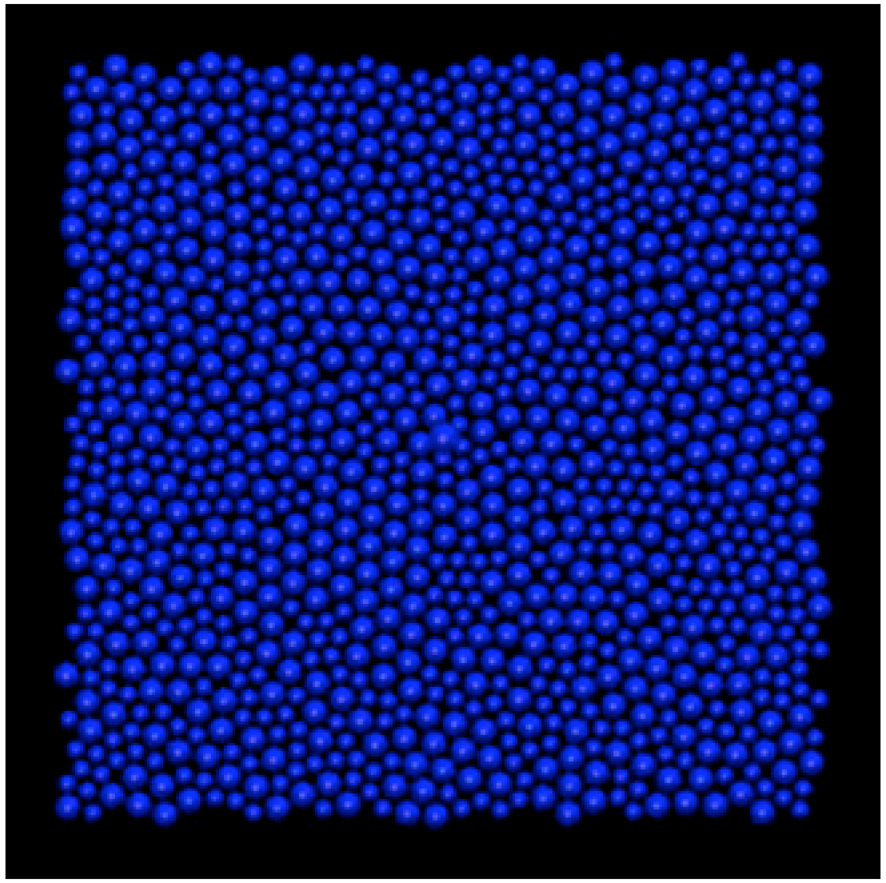

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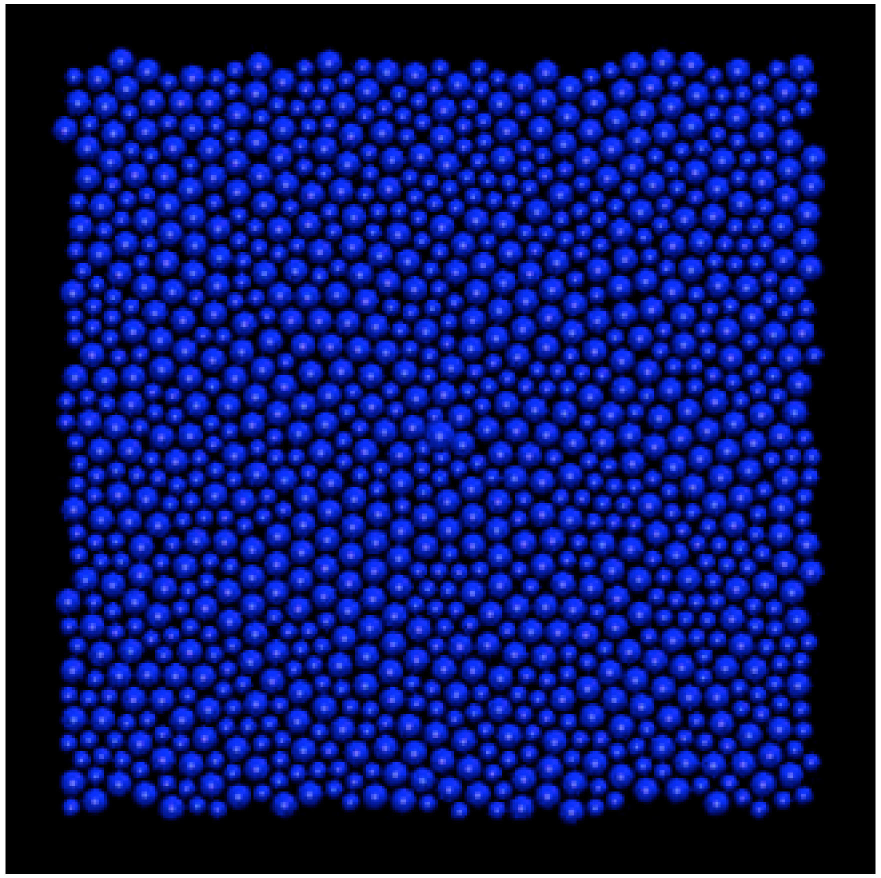

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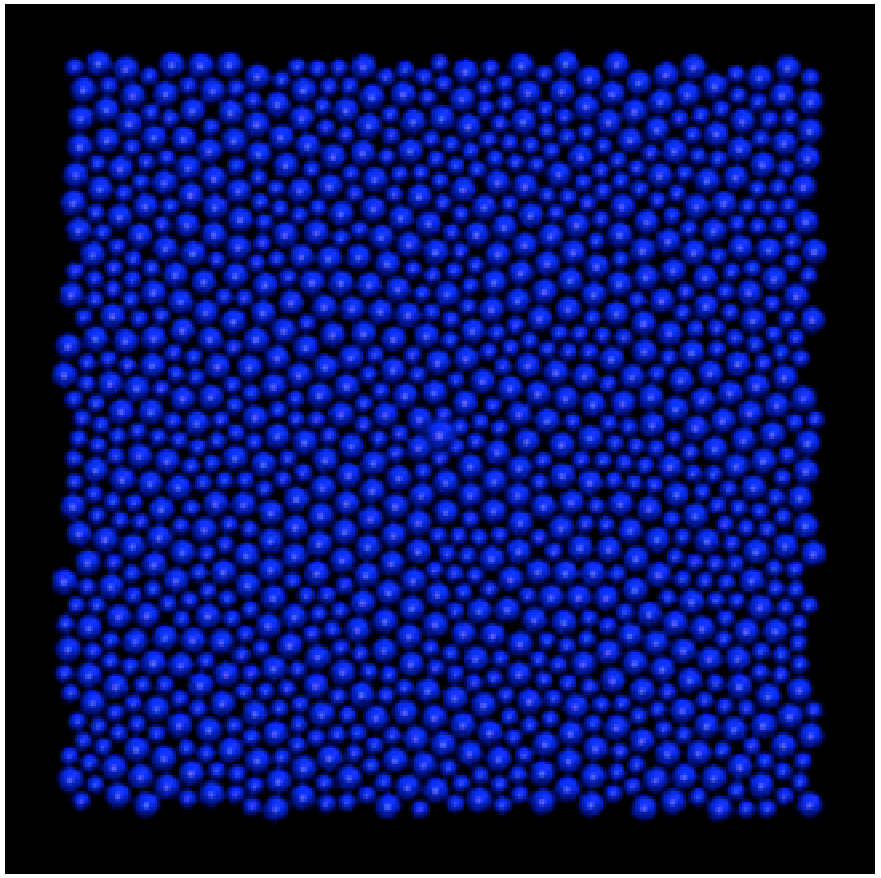

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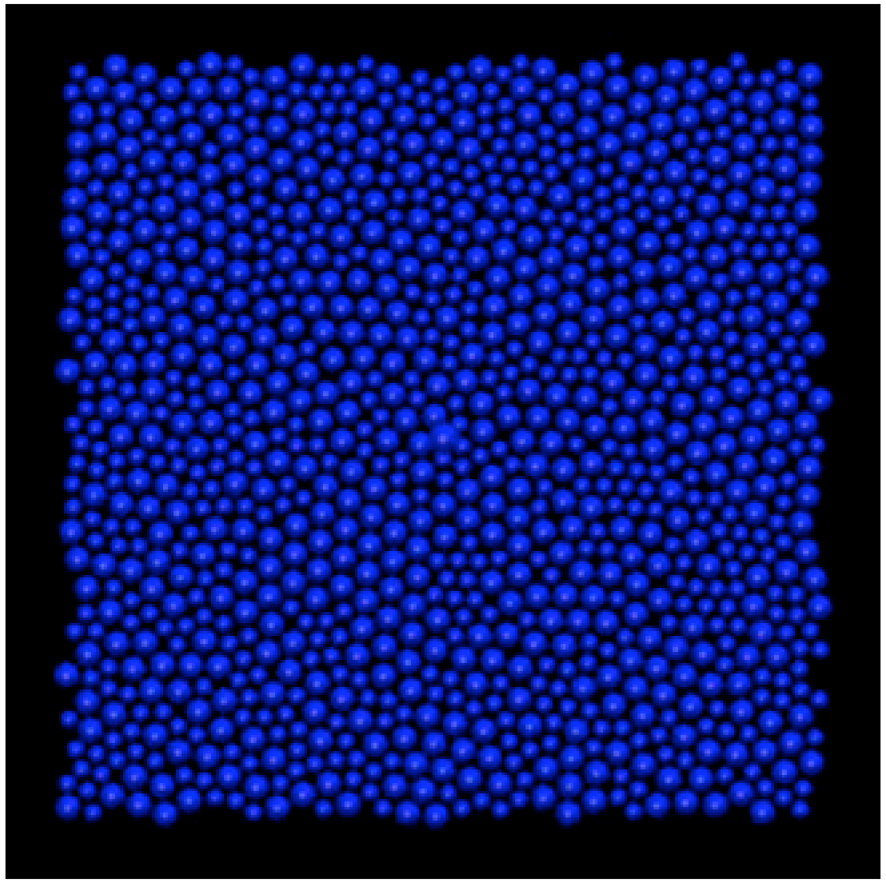

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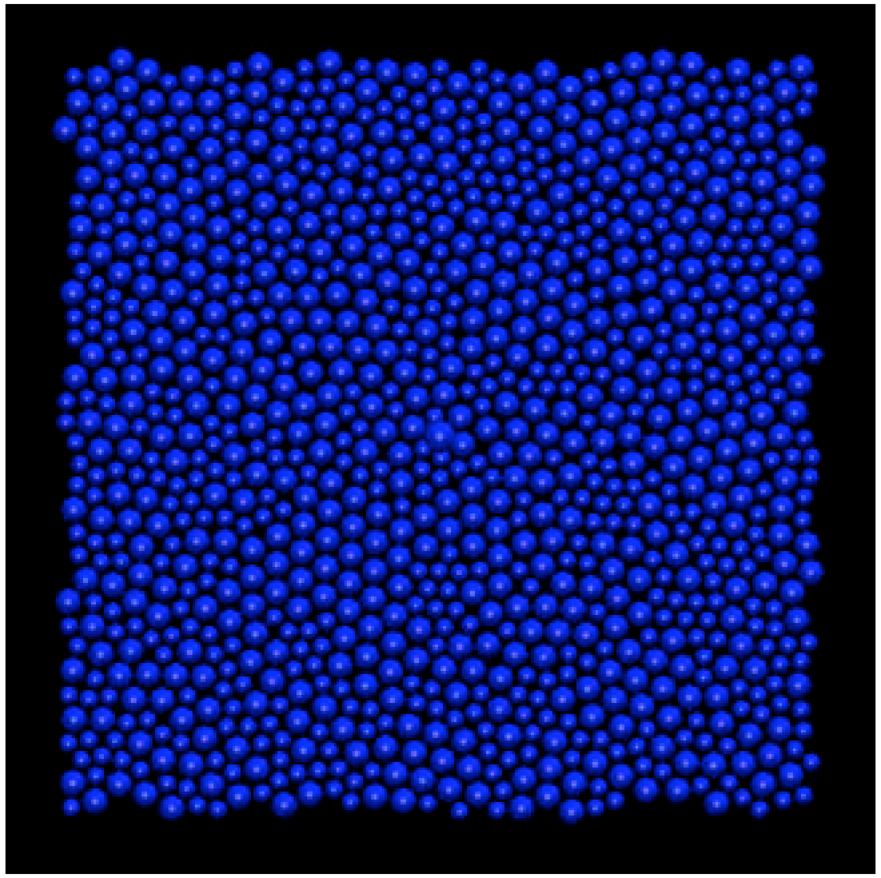

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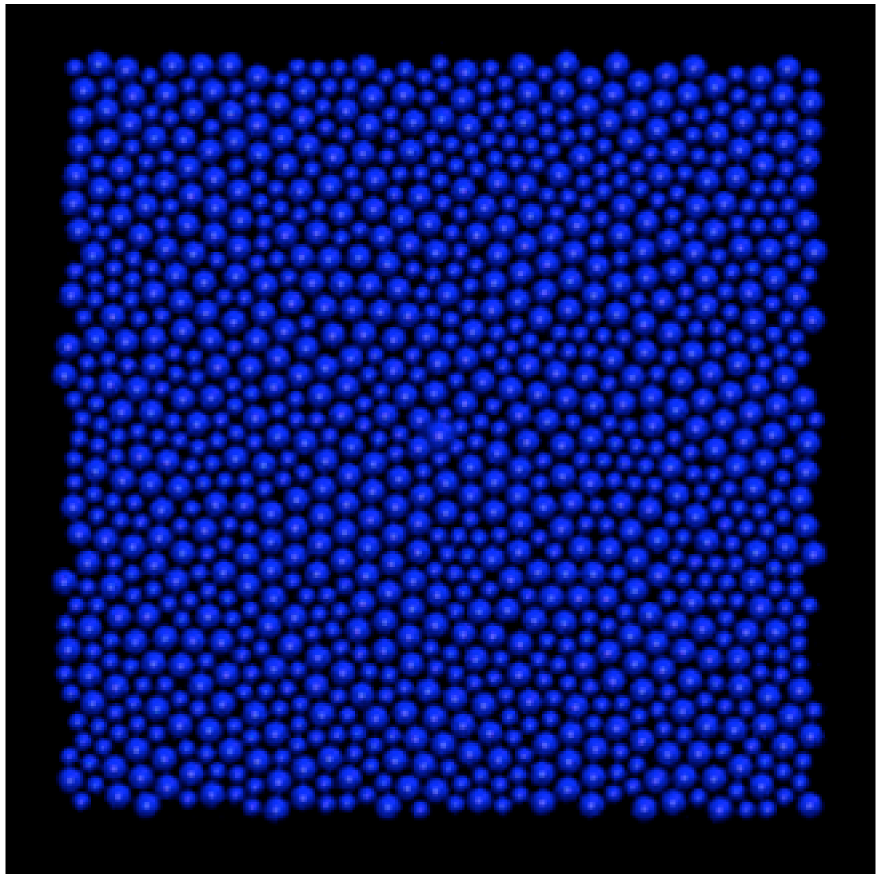

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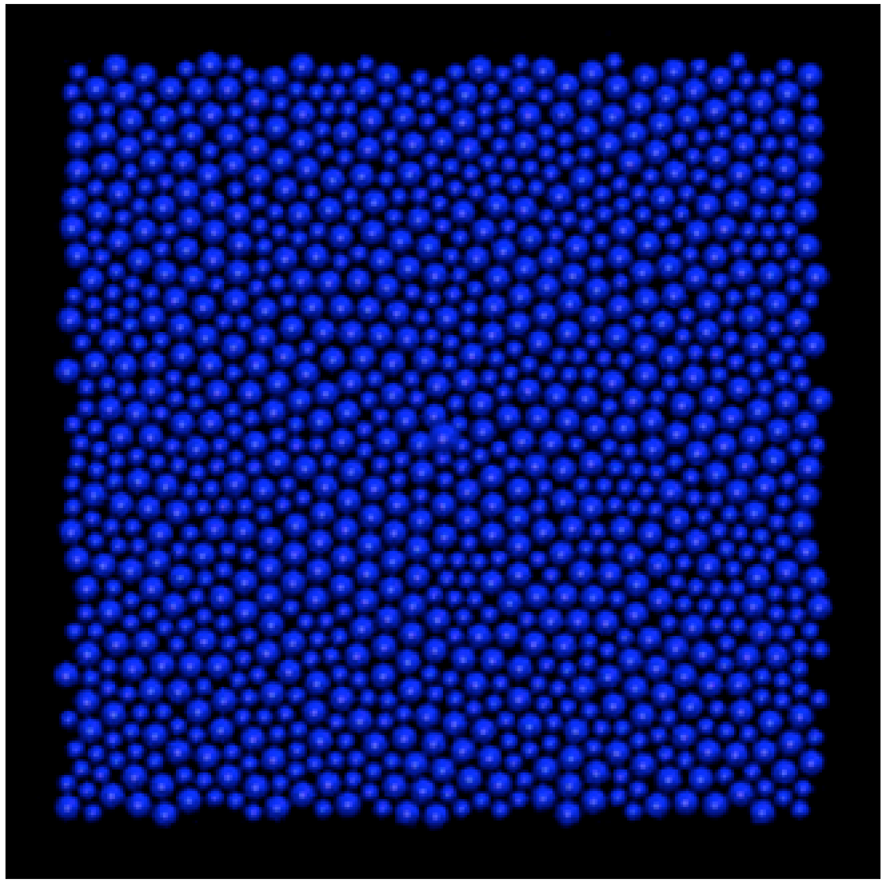

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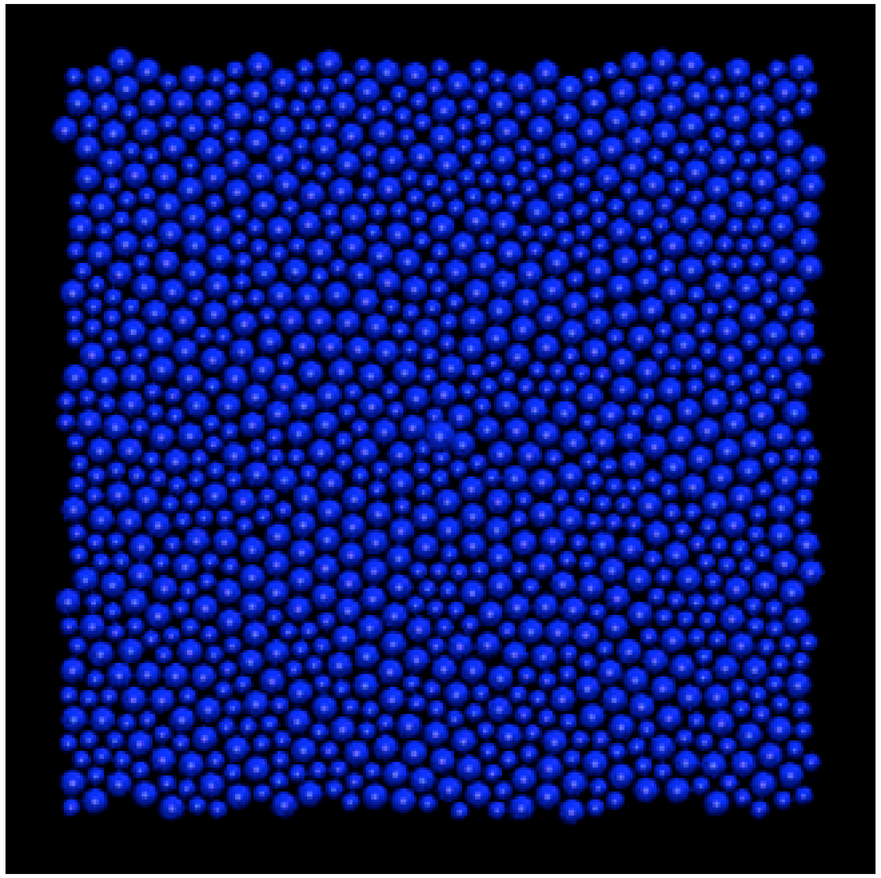

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Excitation density in transition path ensemble

$\mu(\mathbf{r},t)$ = density of other displaced particles with tagged particle at origin

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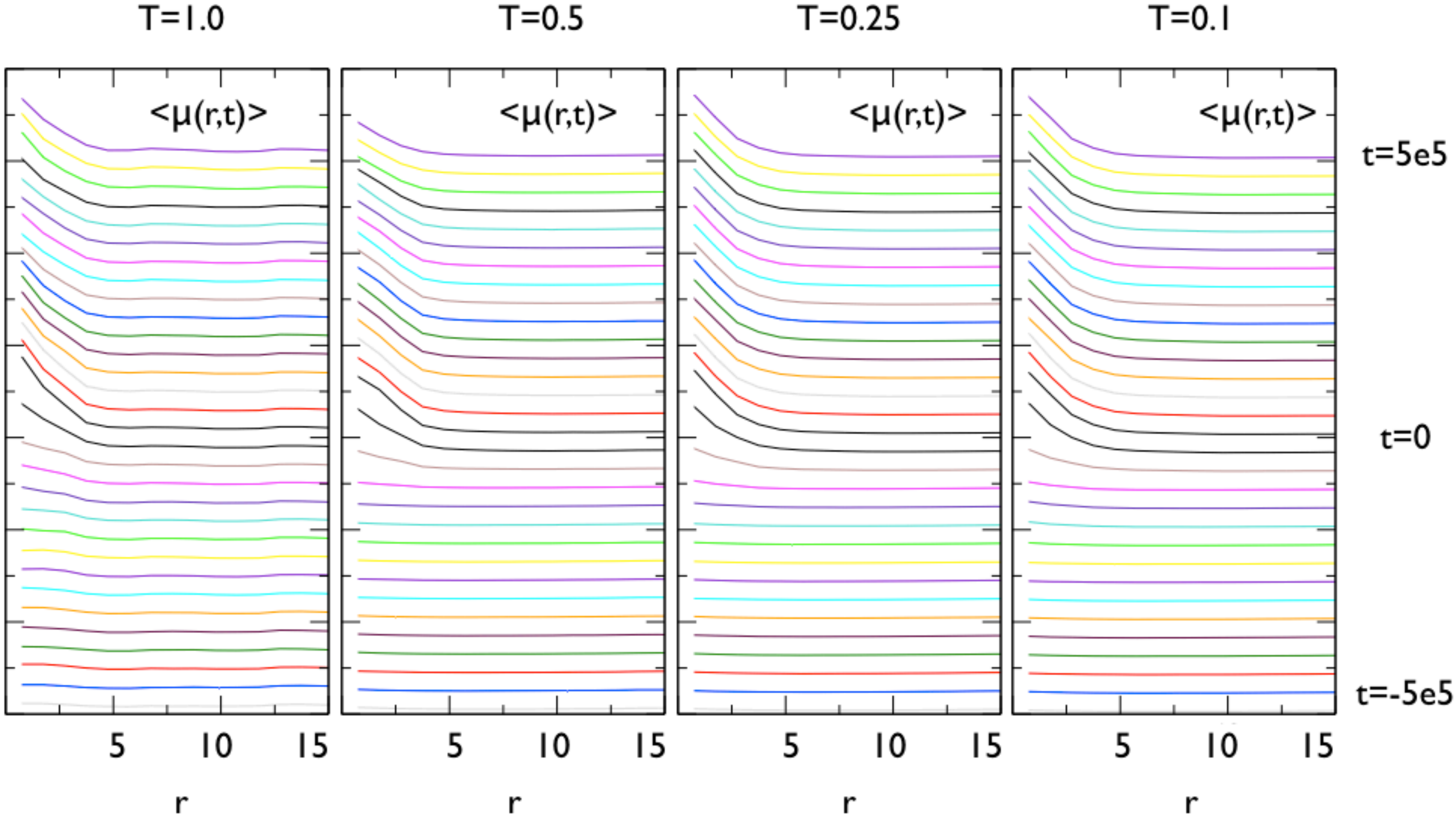

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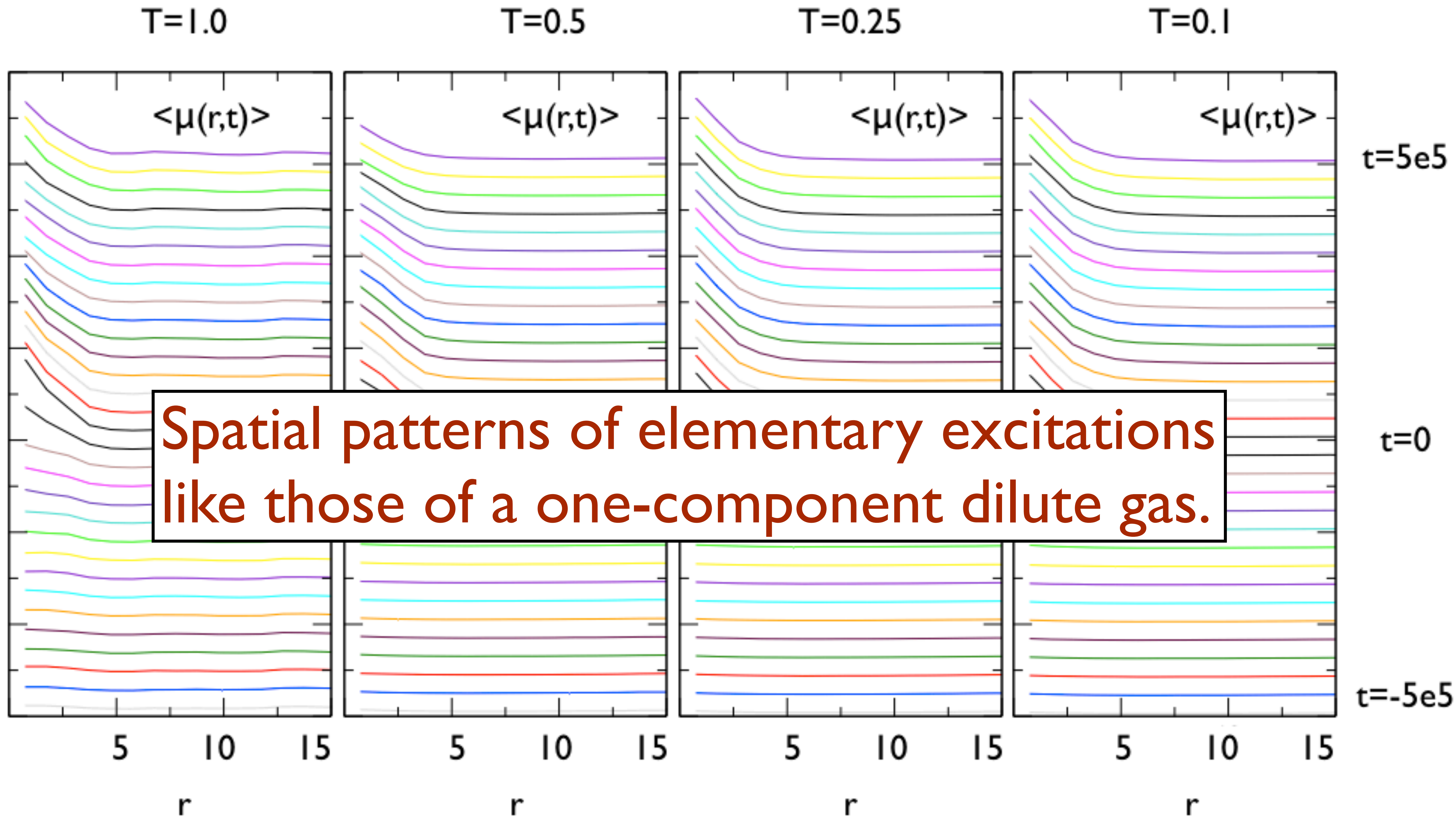

Growing length and time scales

Growing length scale from decreasing mobility excitation concentration, *c*,

$$\ell = c^{-1/d}$$

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e.g., East model and arrow model,

$$\tau \sim c^{\ln c}$$

Consistent temperature dependence of transport & excitations

Mean excitation concentration

$$c \propto \langle \mu(r) \rangle, \quad r \to \infty$$

Arrow model (Garrahan & Chandler, *PNAS* '03)

$$c \propto \exp\left[-J\left(\frac{1}{T}-\frac{1}{T_o}\right)\right] \quad \Rightarrow \quad \frac{\tau}{\tau_o} = \exp\left[J^2\left(\frac{1}{T}-\frac{1}{T_o}\right)^2\right] \quad , \quad T \le T_o$$

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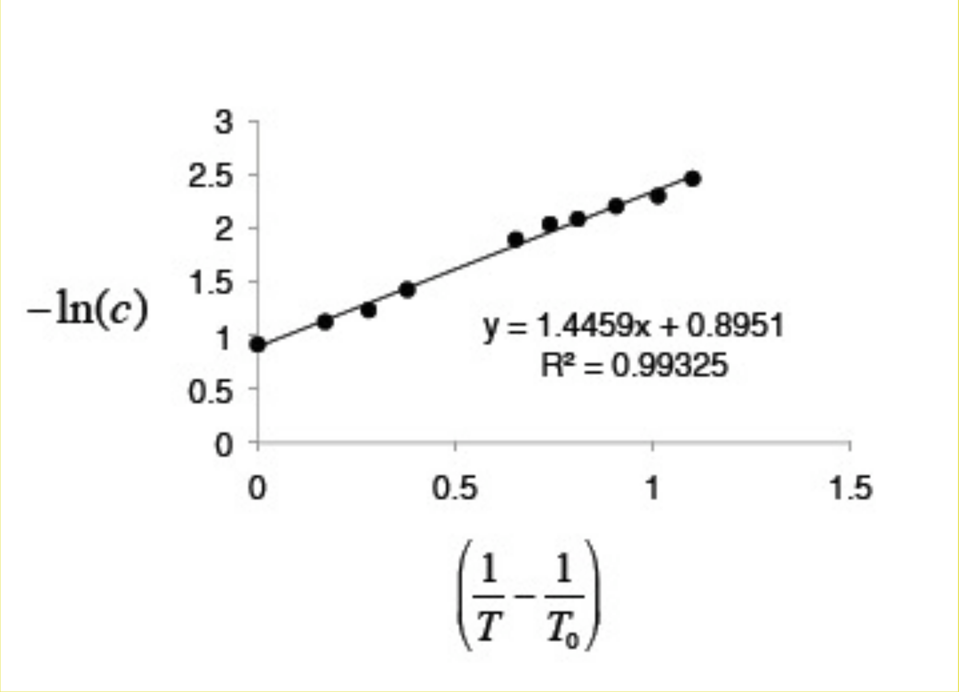
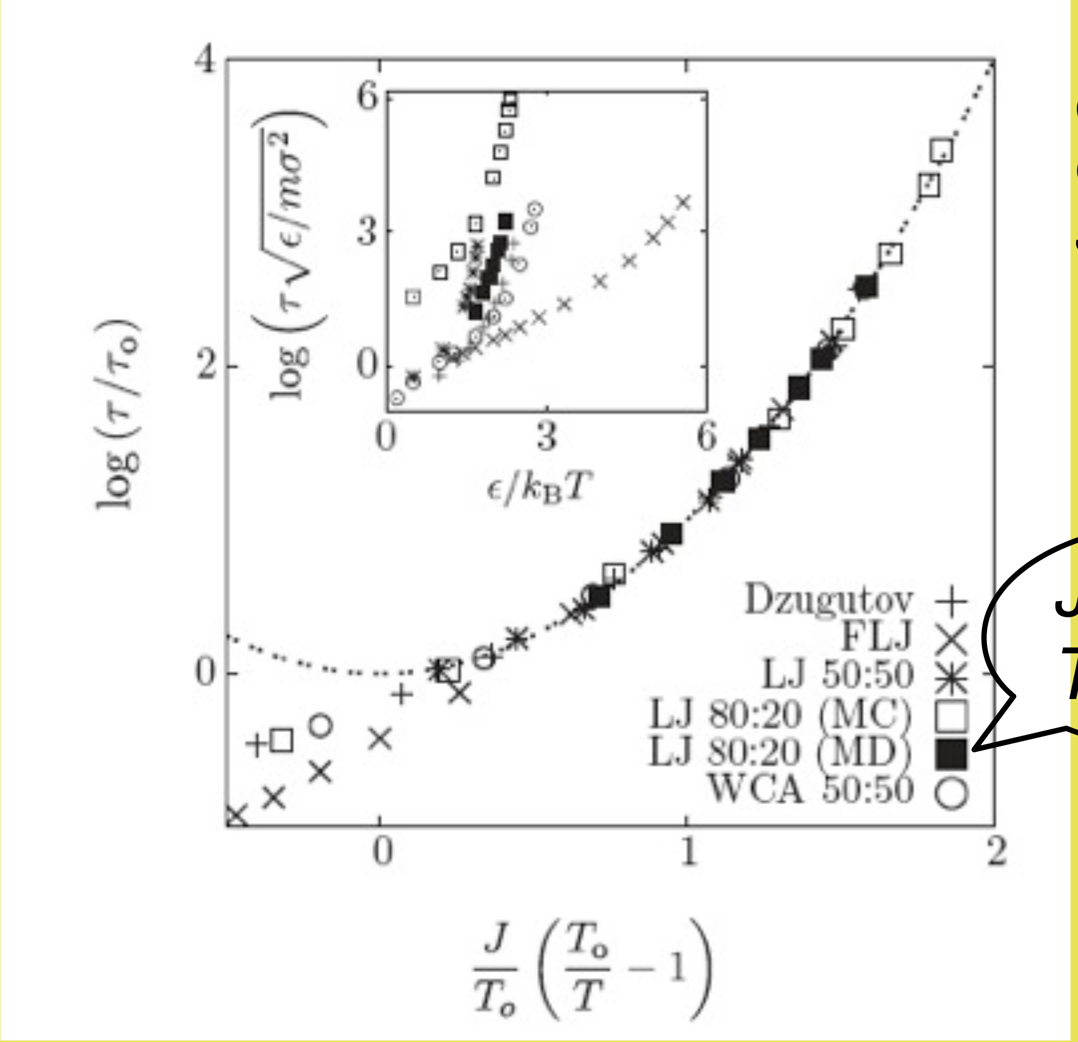
Kob-Andersen 80:20 LJ mixture, $d = 3$.

MD simulation with N = 10,000, $\rho\sigma^3 = 1.2$

Keys, Hedges, Glotzer & Chandler, in prep, '10



$$[J]_{\text{from } c} \approx 1.45, \quad [T_o]_{\text{from } c} \approx 0.90$$

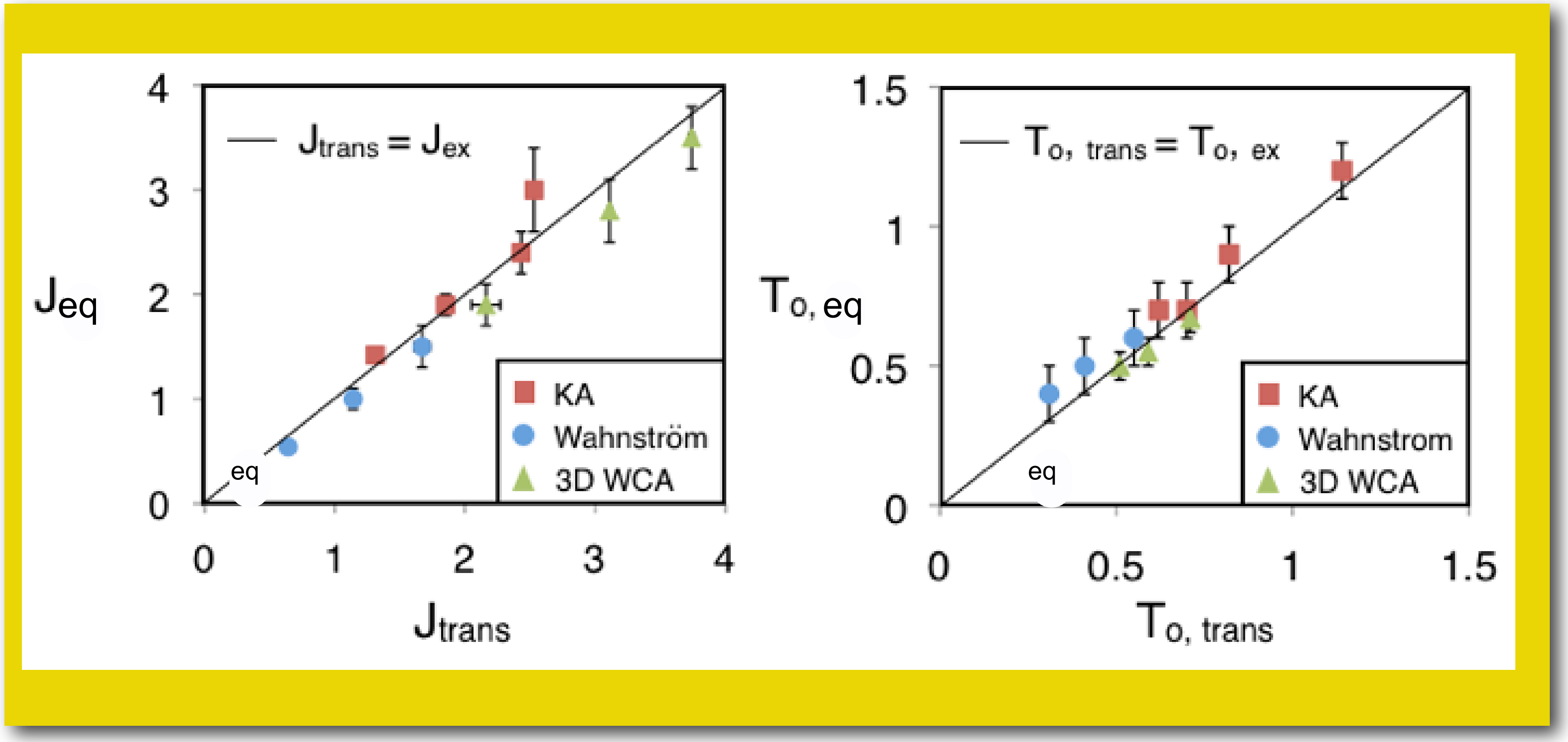


Elmatad, Chandler & Garrahan, *J.Phys. Chem.B*'09

$J = 1.5$
$T_o = 0.9$

Equilibrium & transport J's and T_o's

$$c \propto \exp\left[-J_{\rm eq}\left(\frac{1}{T}-\frac{1}{T_{\rm o,\,eq}}\right)\right], \qquad \tau \propto \exp\left[J_{\rm trans}^2\left(\frac{1}{T}-\frac{1}{T_{\rm o,\,trans}}\right)^2\right]$$

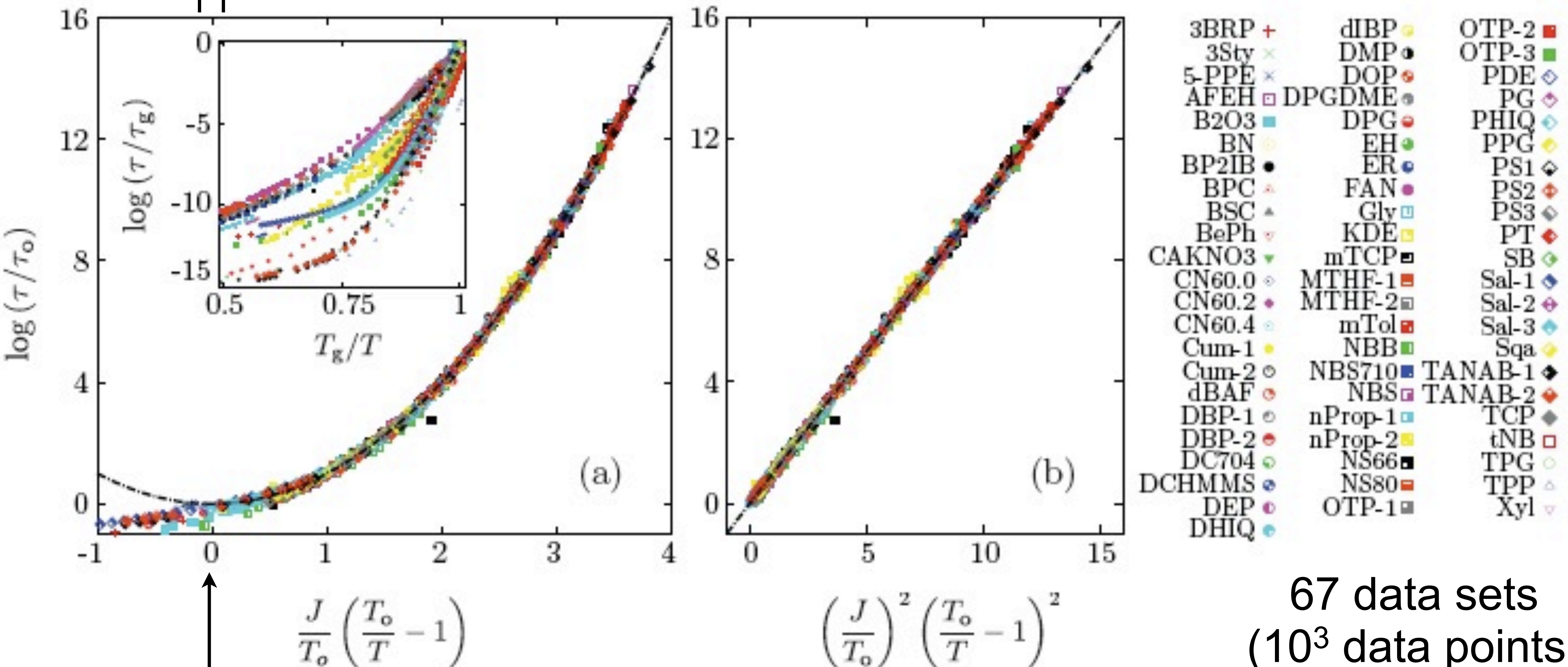


Keys, Hedges, Glotzer & Chandler, in prep, '10

Transport data quadratic data collapse below onset temperature

Elmatad, Chandler & Garrahan, *J. Phys. Chem. B* (2009)

normal ← → supercooled



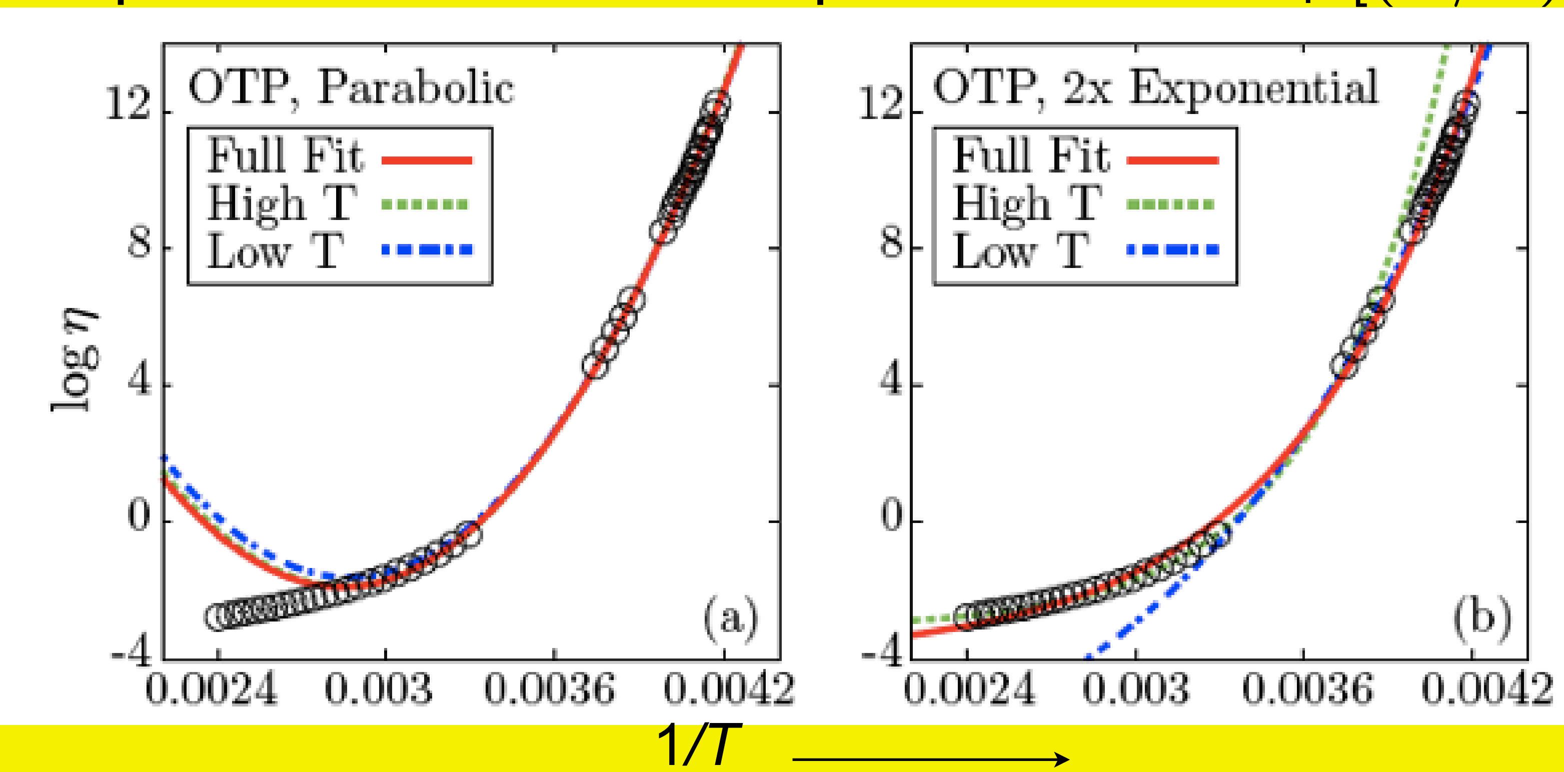
67 data sets
(10^3 data points)

onset temperature

Material properties J and T_o

not so for other functional form parameters

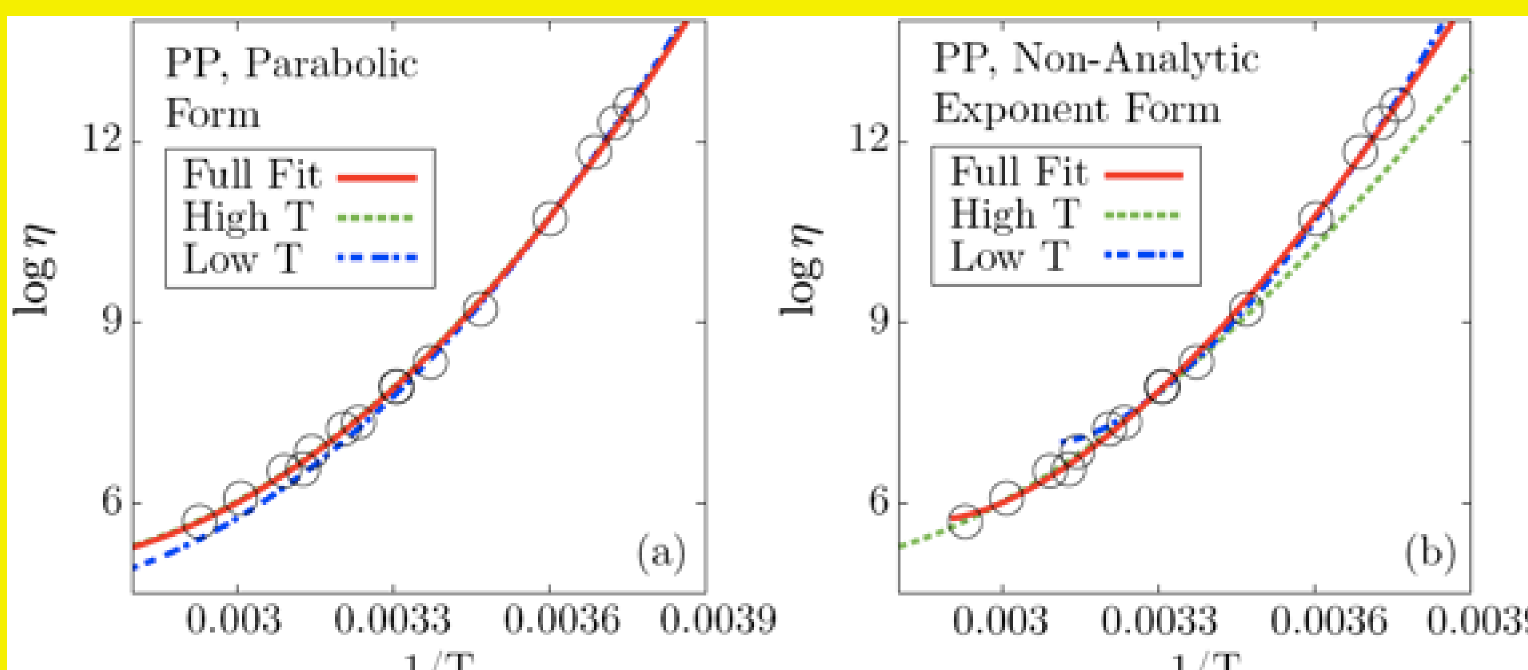
Example: OTP and double exponential $\tau \propto \exp\left[(K/T)\exp(C/T)\right]$



	high T	low T	all $T<T_o$
T_o	351	350	352
J/T_o	8.0	8.1	7.9
K	1.34	203	15.7
C	1.96×10^3	769	1.32×10^3

Example: PP and non-analytic exponent $\tau \propto \exp\left[X(T_c/T-1)^{1.57}\right]$

	high T	low T	all $T<T_o$
T_o	392	397	392
J/T_o	5.8	5.7	5.8
T_c	370	322	346
X	29	67	45



Large deviation functions (Gibbs)

& equilibrium phase transitions

$$\rho(x) \;\rightarrow\; \rho(x)\, e^{-rA(x)} / Z_r\,, \qquad Z_r = \sum_x \rho(x)\, e^{-rA(x)} \equiv e^{-\beta F_r}$$

$$P_r(A) \;\propto\; \sum_x \rho(x)\, e^{-rA(x)} \delta\big(A - A(x)\big)$$

$$= P_0(A)\, e^{-rA}$$

A = extensive order parameter

r = thermodynamic field,
conjugate to A

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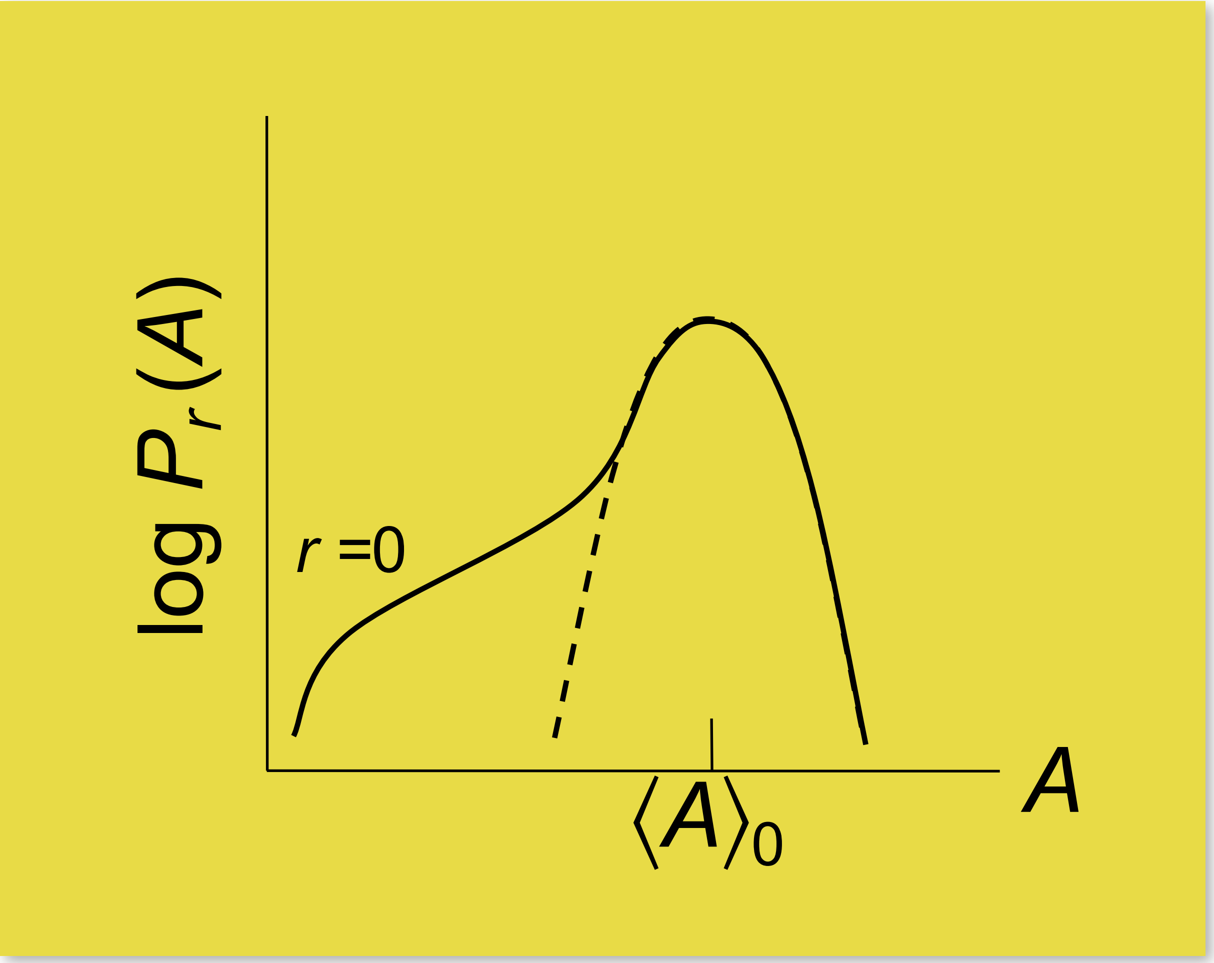

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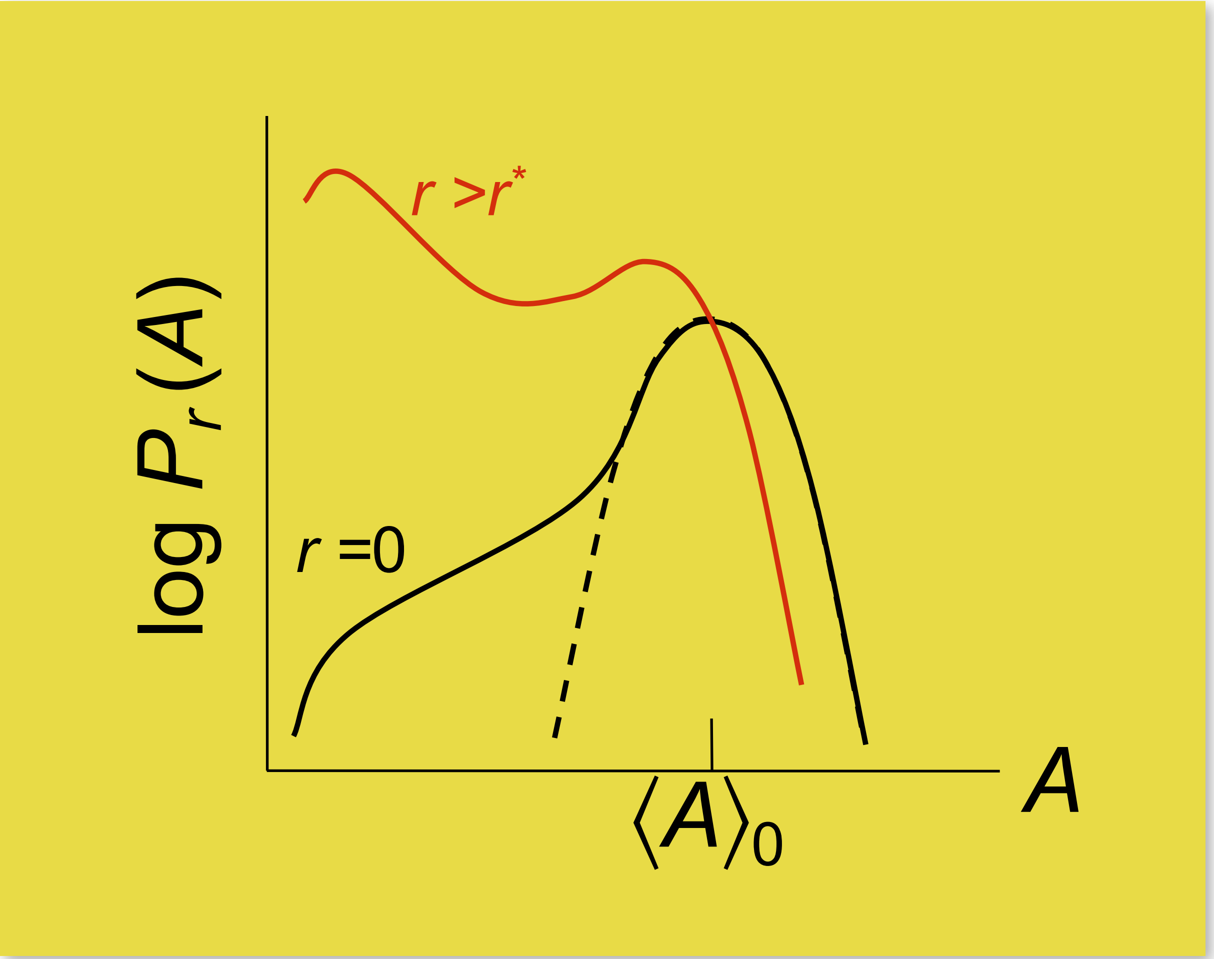

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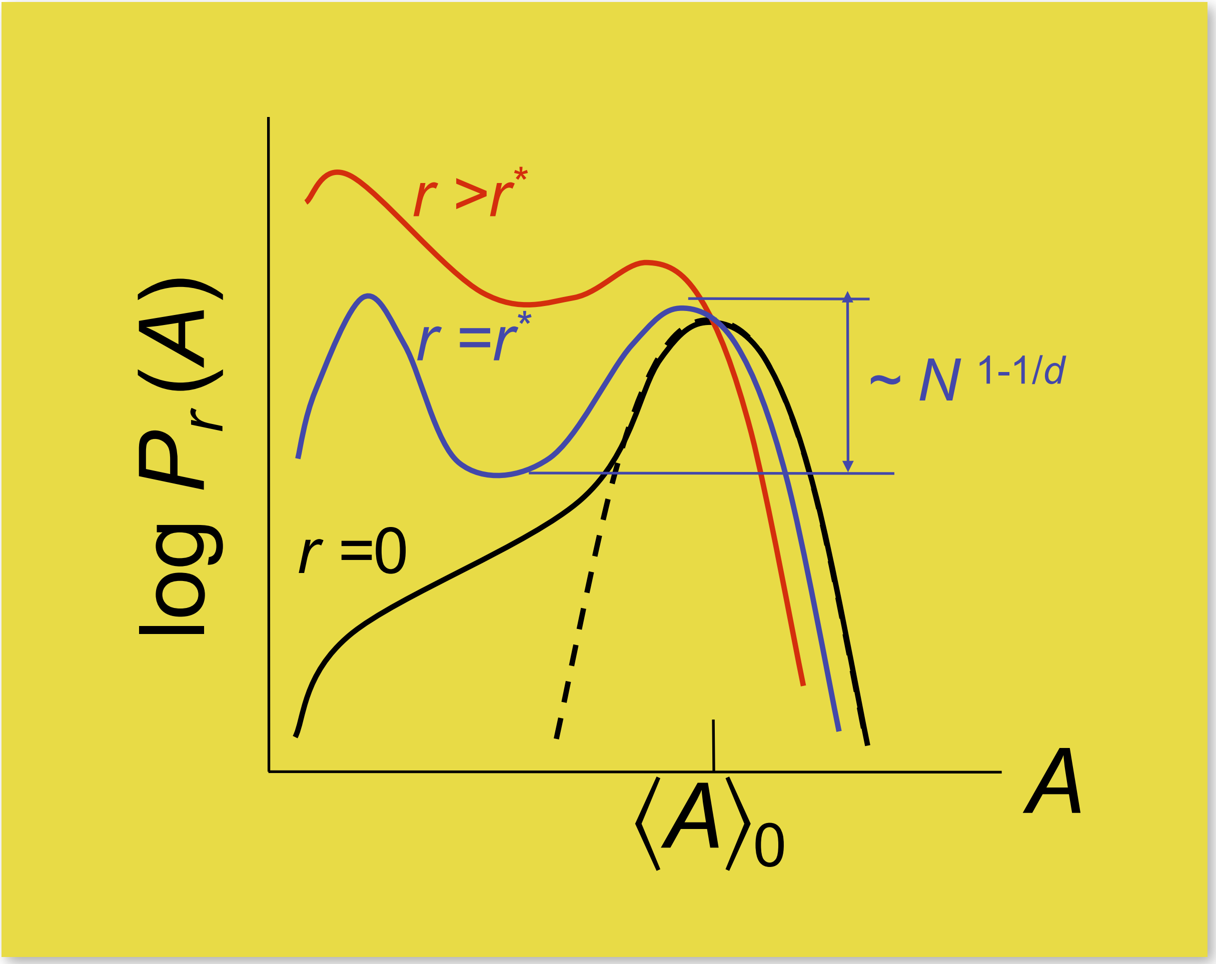

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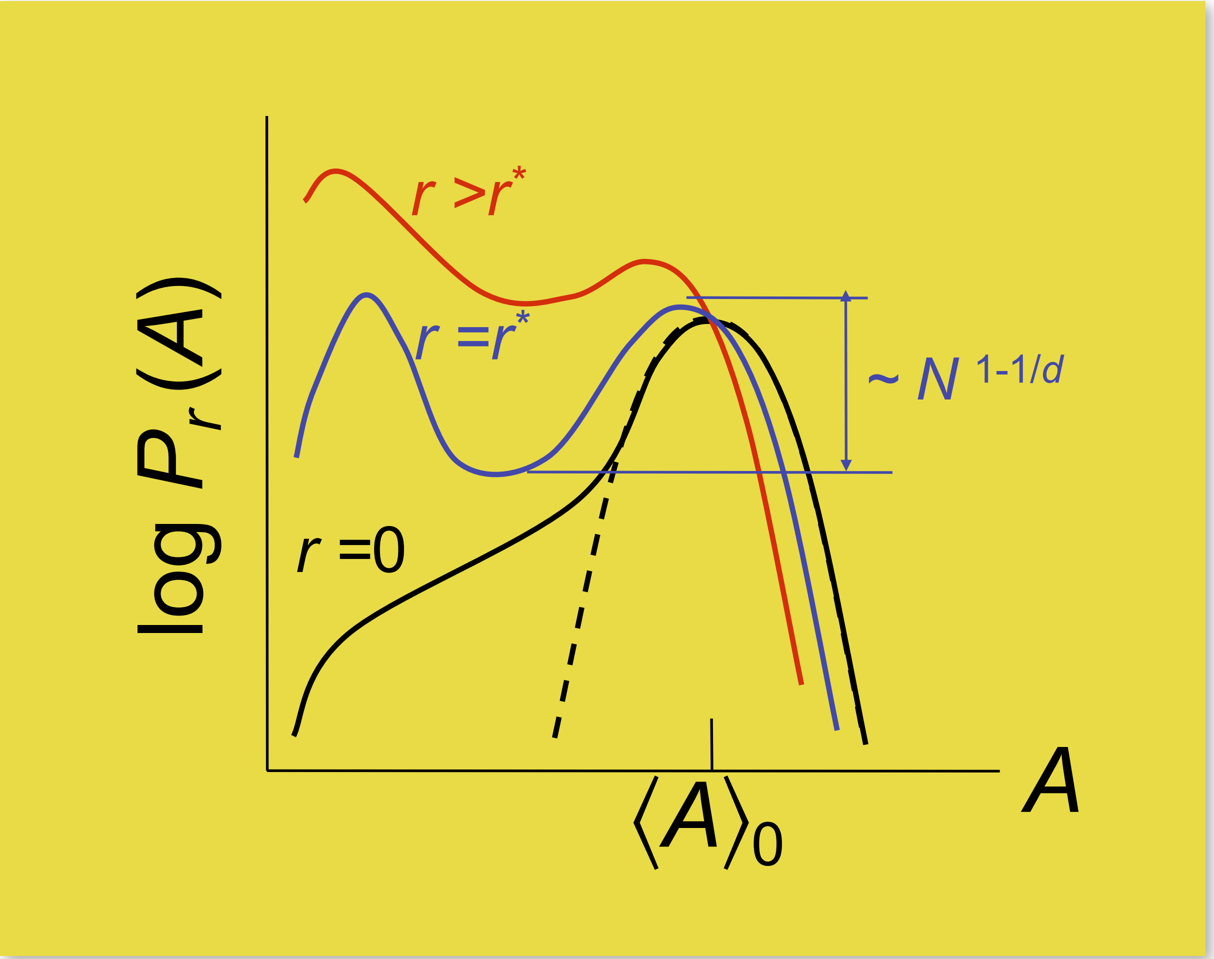

$r = r^*$, $\langle A \rangle_r$ discontinuous $\Rightarrow$ coexistence

Large deviation functions (Ruelle), & dynamic phase transitions

$$P\left[x(t)\right], \quad x(t) = (x_0, x_1, \ldots, x_t, \ldots, x_{t_{\mathrm{obs}}})$$

$$P\left[x(t)\right] \quad \rightarrow \quad P_s\left[x(t)\right] \propto P\left[x(t)\right] \exp\left(-sK\left[x(t)\right]\right)$$

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Harvest with transition path sampling

Merolle, Garrahan & Chandler, *PNAS* (2005)

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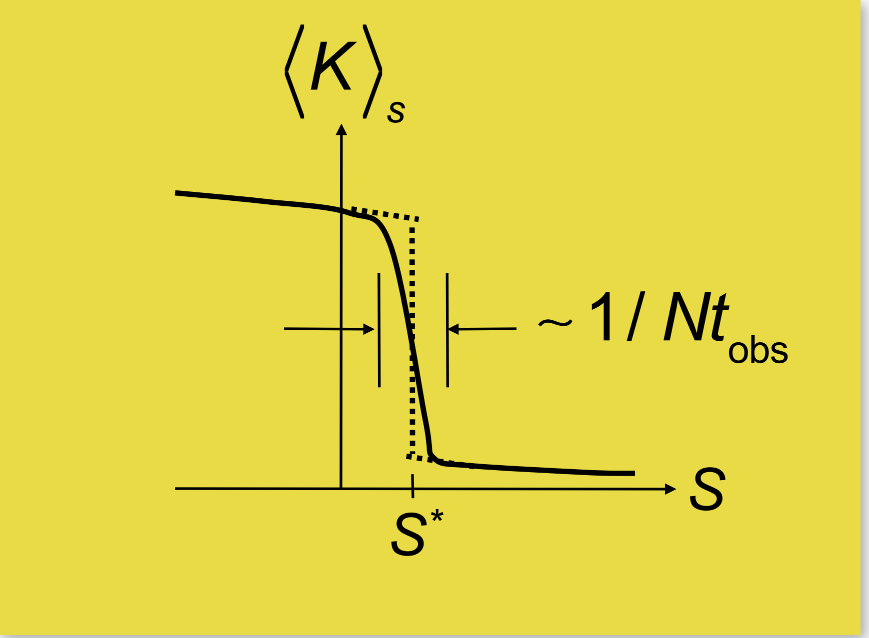
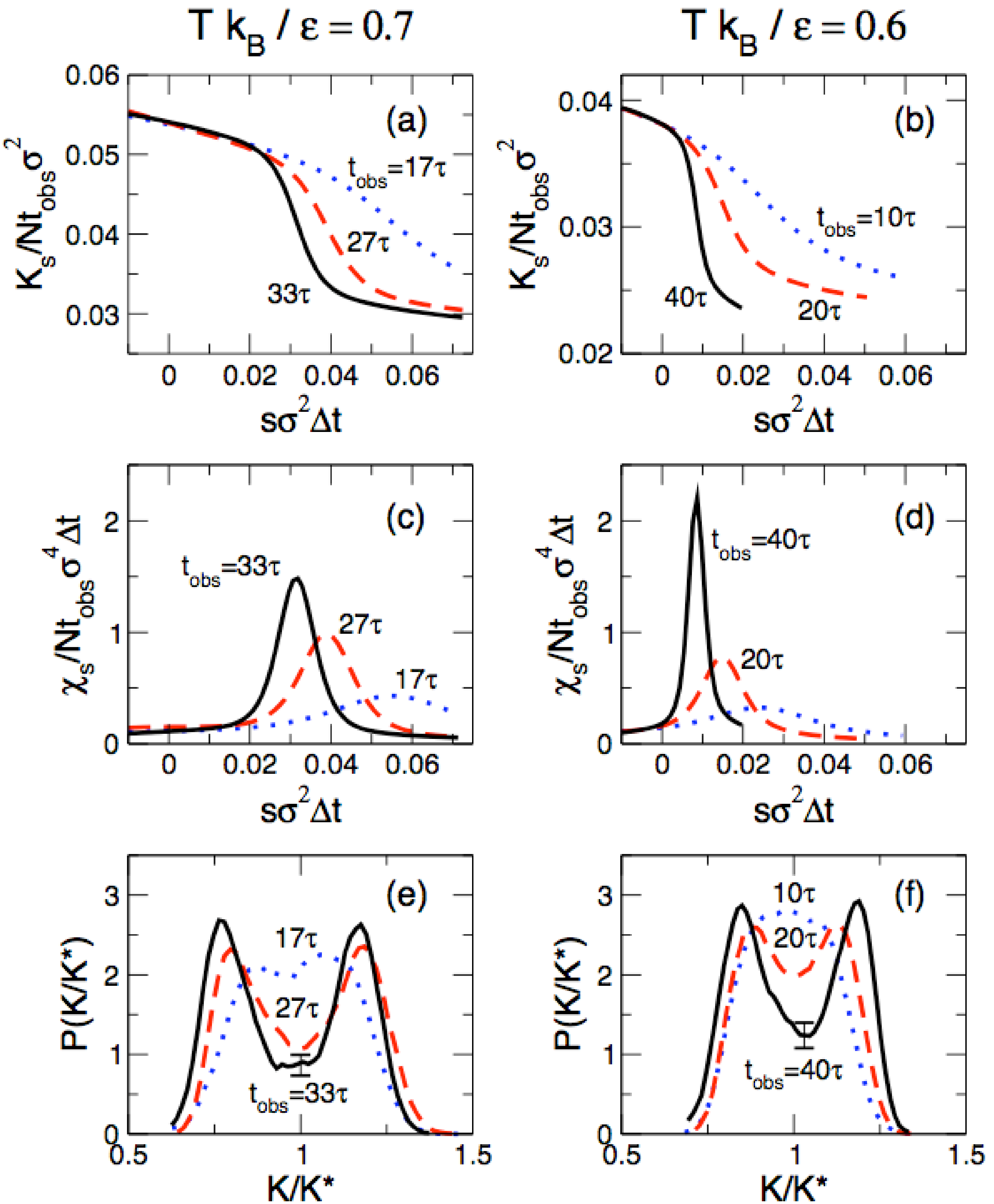
Merolle, Garrahan & Chandler, *PNAS* (2005)

& if there is order-disorder associated with activity →



Evidence of First-order Phase Transition

In Kob-Andersen (80:20 LJ) super-cooled liquid mixture



Hedges et al. *Science* (2009)

N =200

τ = structural relaxation time

≈ 15 & 45 Δt

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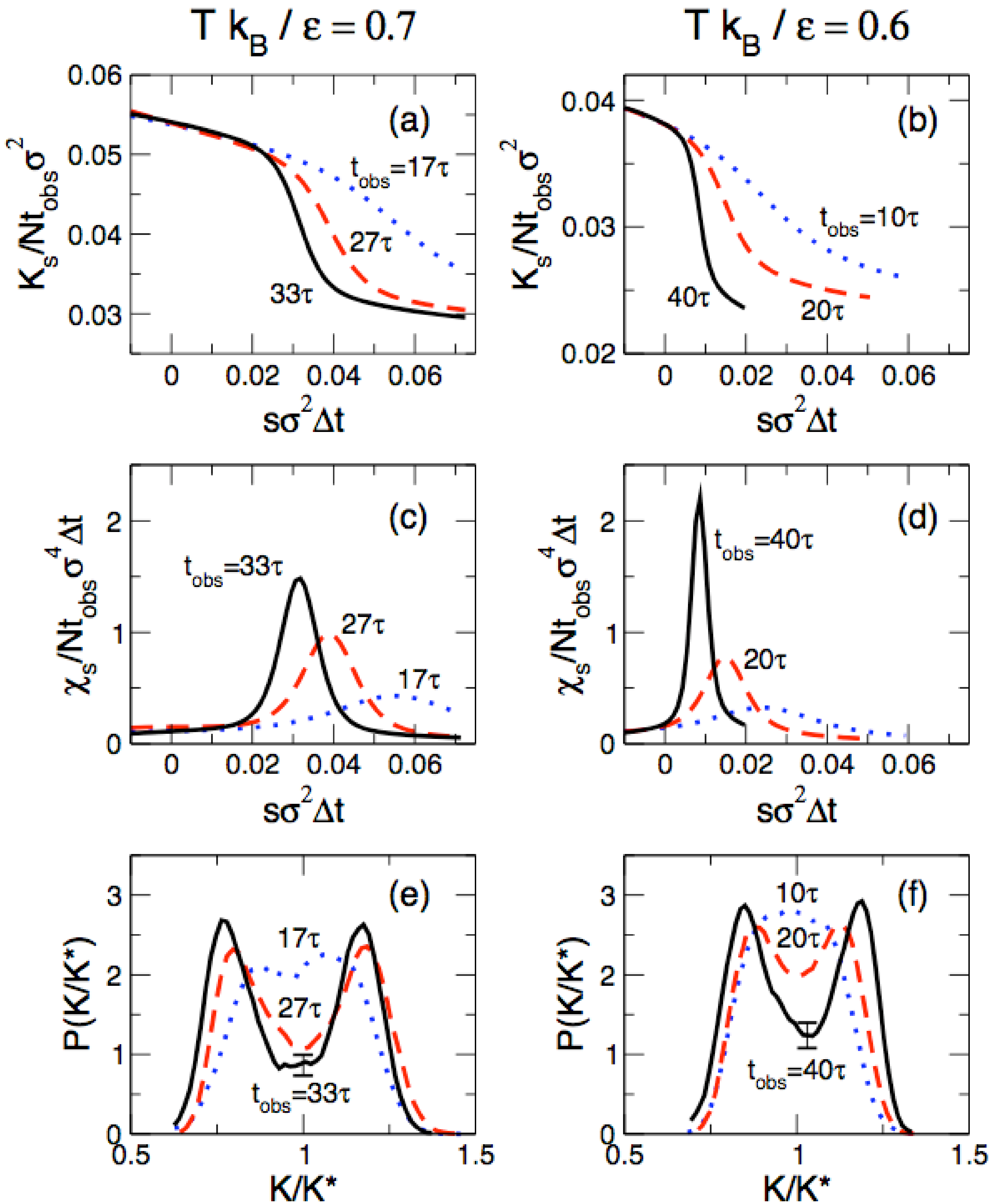
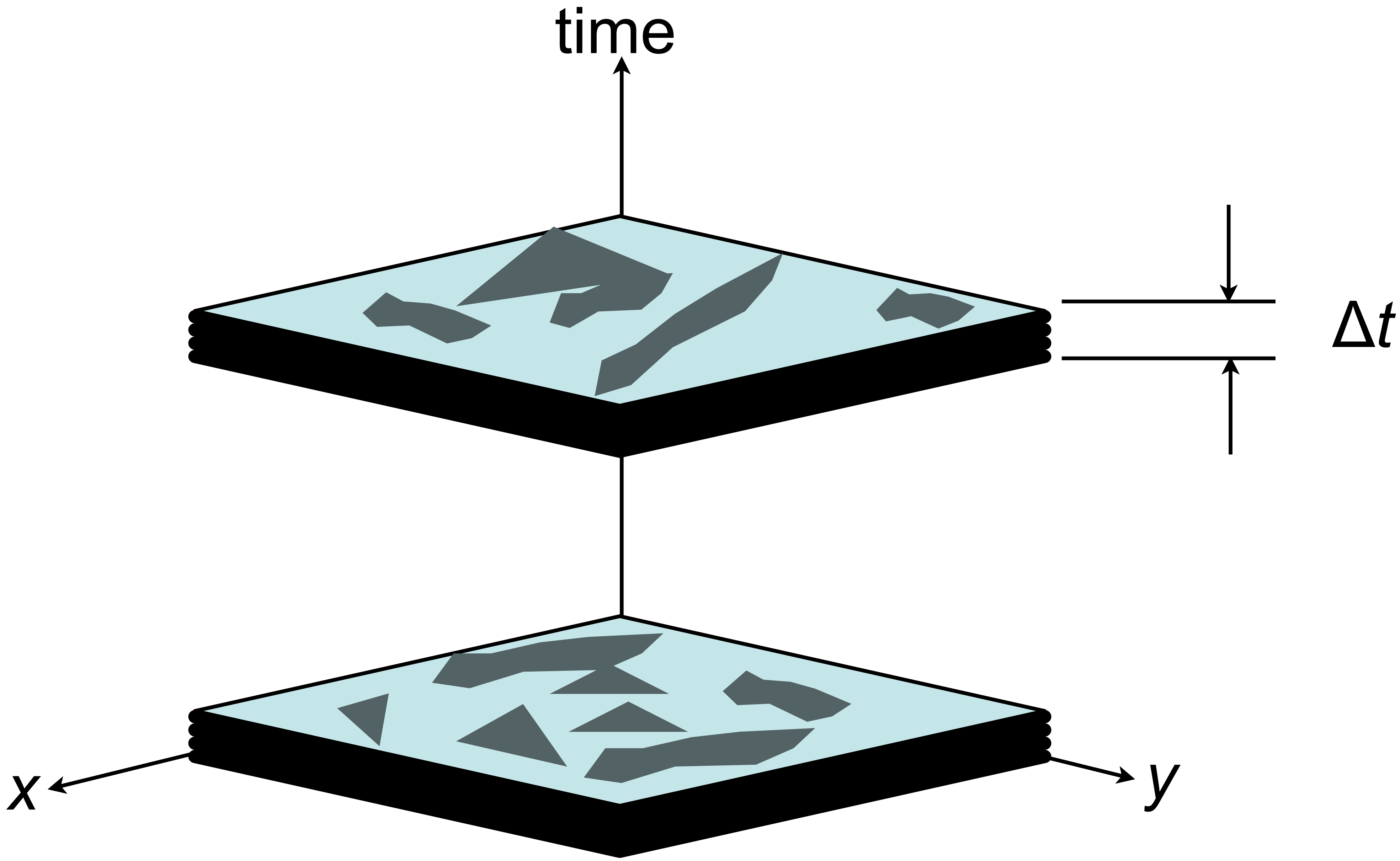


Not χ_4

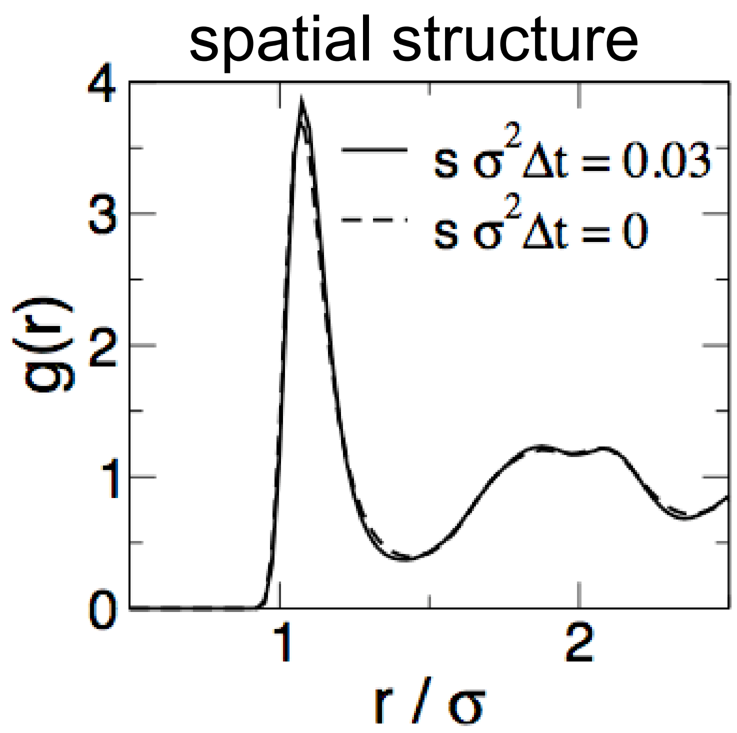
χ_4 refers to <u>plane</u> in space-time, not <u>volume</u>.

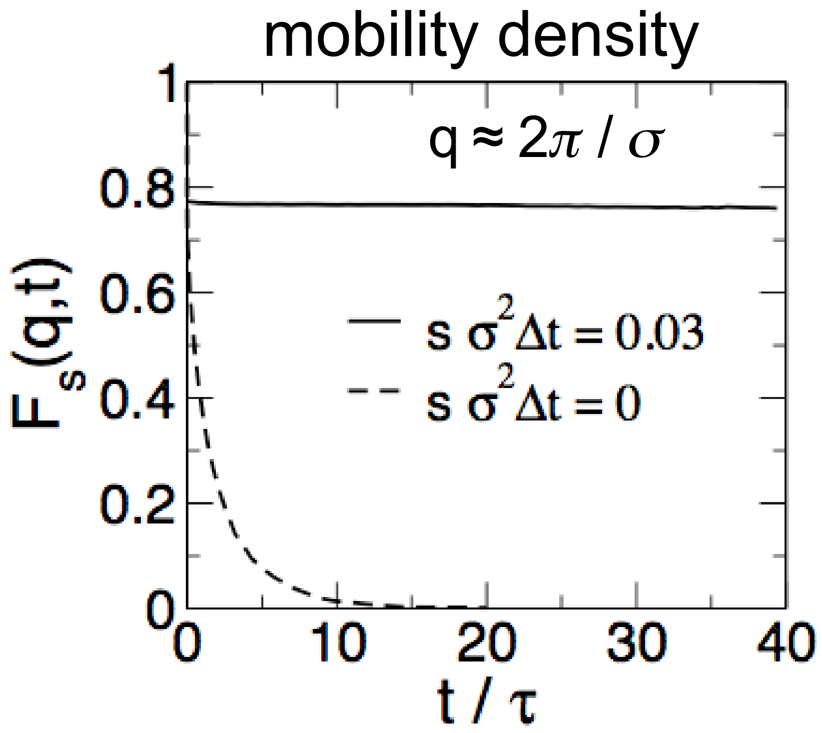


Space-time Structure & Coexistence

Hedges et al.
Science (2009)

$T\,k_B / \varepsilon = 0.6, \; 0 < s^* < 0.03$





$$g(r) \propto \sum_{1<i\leq N} \left\langle \delta(r_i - r)\delta(r_1) \right\rangle_s \qquad F_s(q,t) = \frac{1}{N} \sum_{1\leq i\leq N} \left\langle e^{iq\cdot[r_i(t)-r_i(0)]} \right\rangle_s$$

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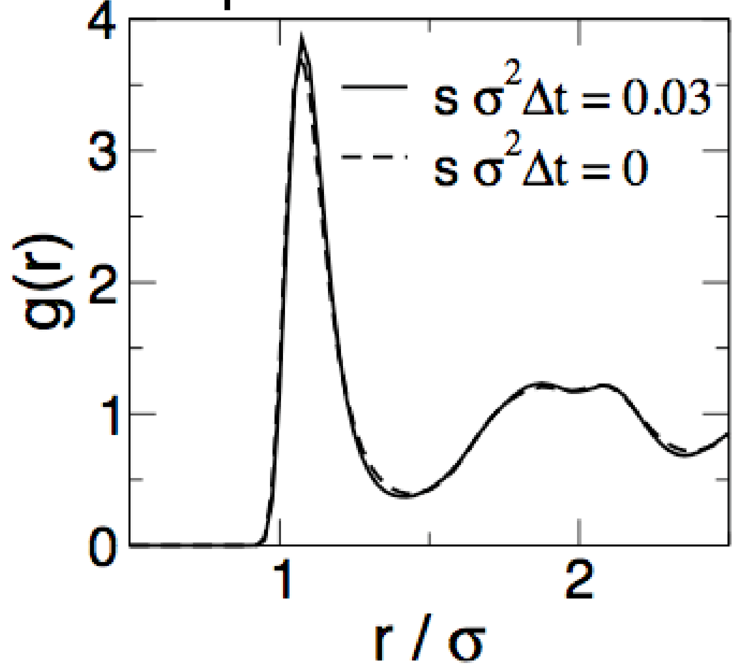
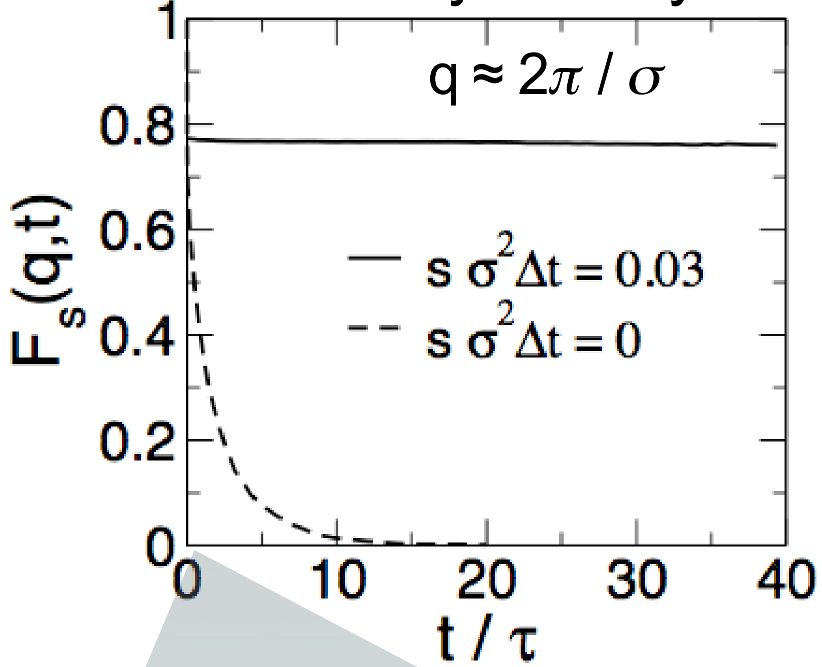
spatial structure

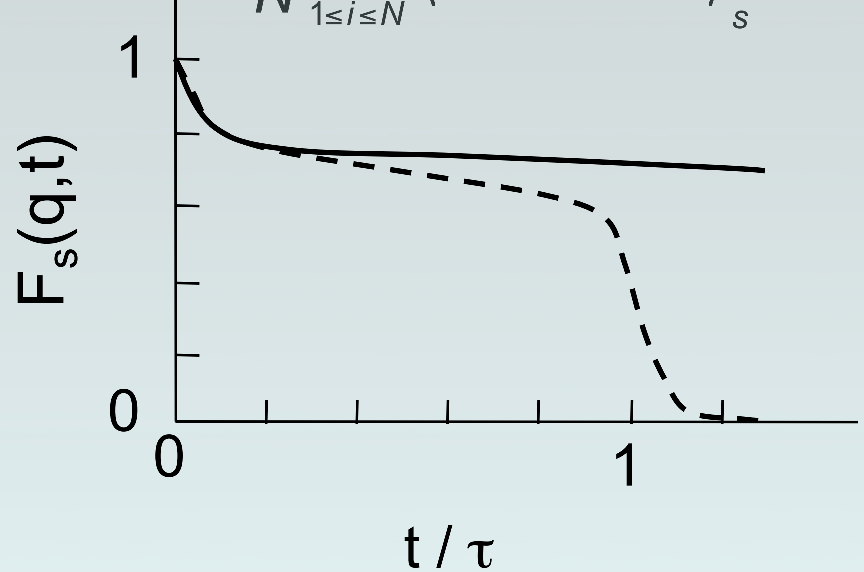


mobility density



$$g(r) \propto \sum_{1<i\leq N} \left\langle \delta(r_i - r)\delta(r_1) \right\rangle_s$$

$$F_s(q,t) = \frac{1}{N} \sum_{1\leq i\leq N} \left\langle e^{iq\cdot[r_i(t)-r_i(0)]} \right\rangle_s$$

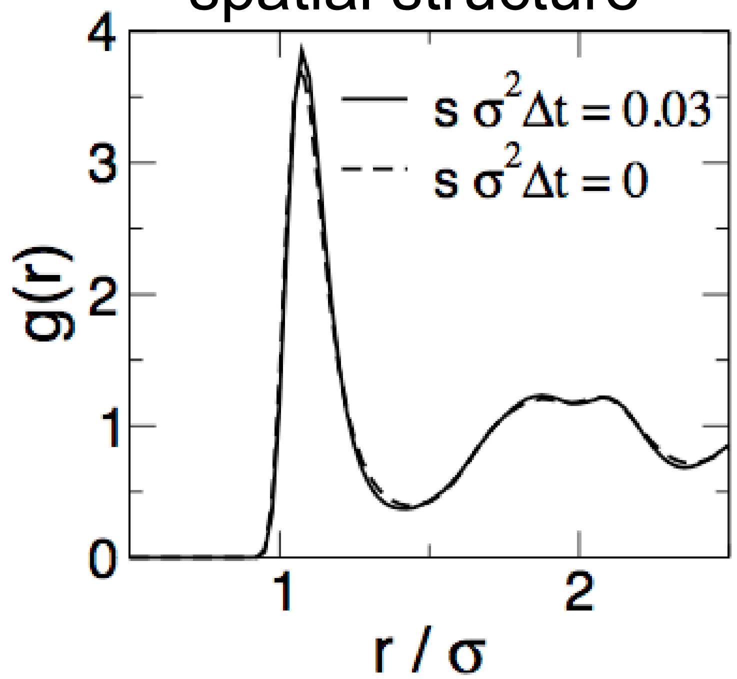


Space-time Structure & Coexistence

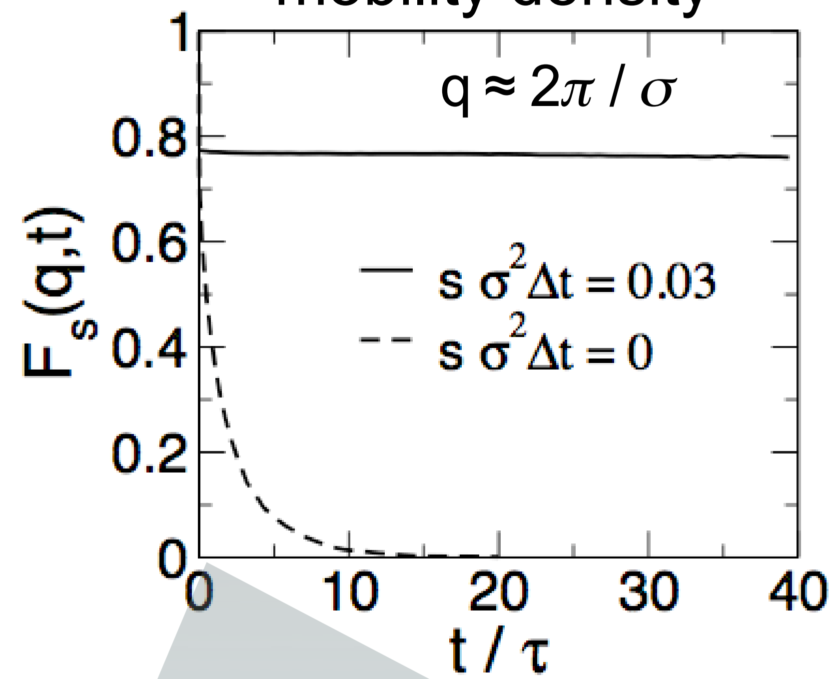
$T\, k_B / \varepsilon = 0.6, \; 0 < s^* < 0.03$

Hedges et al.
Science (2009)

spatial structure



mobility density



$$g(r) \propto \sum_{1<i\le N} \left\langle \delta(r_i - r)\delta(r_1) \right\rangle_s$$

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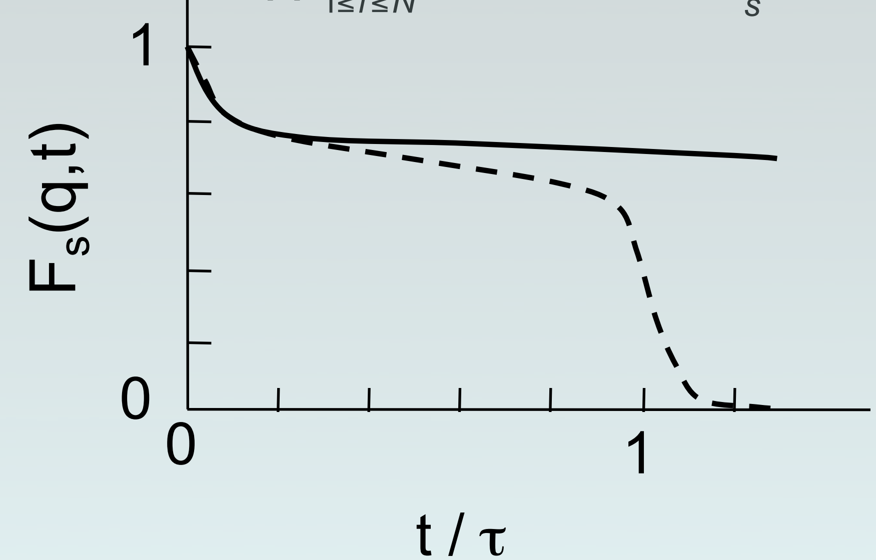
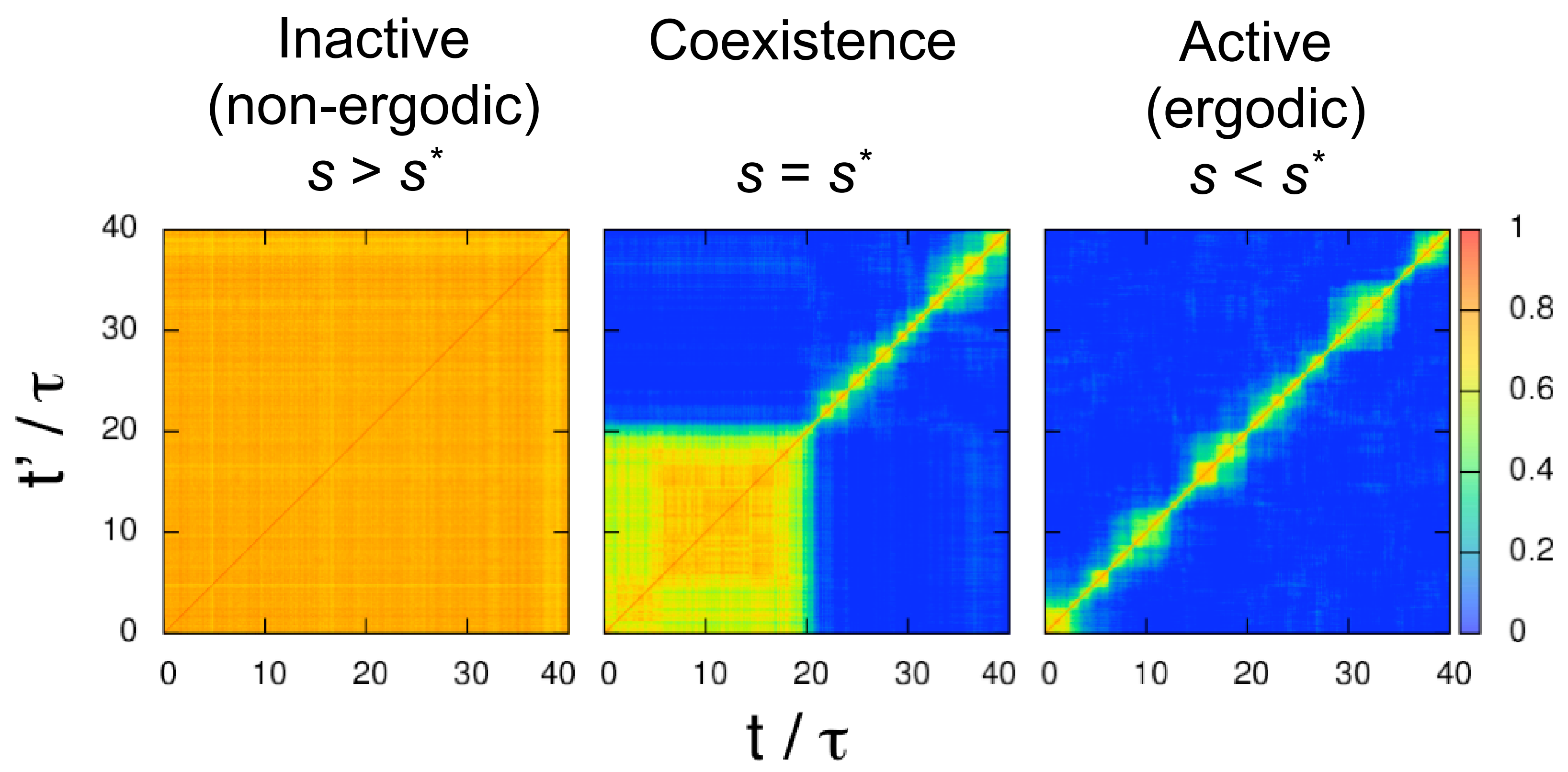


Pre-wetting & wetting of initial conditions

Active-Inactive Coexistence, con'd

Hedges et al.
Science (2009)

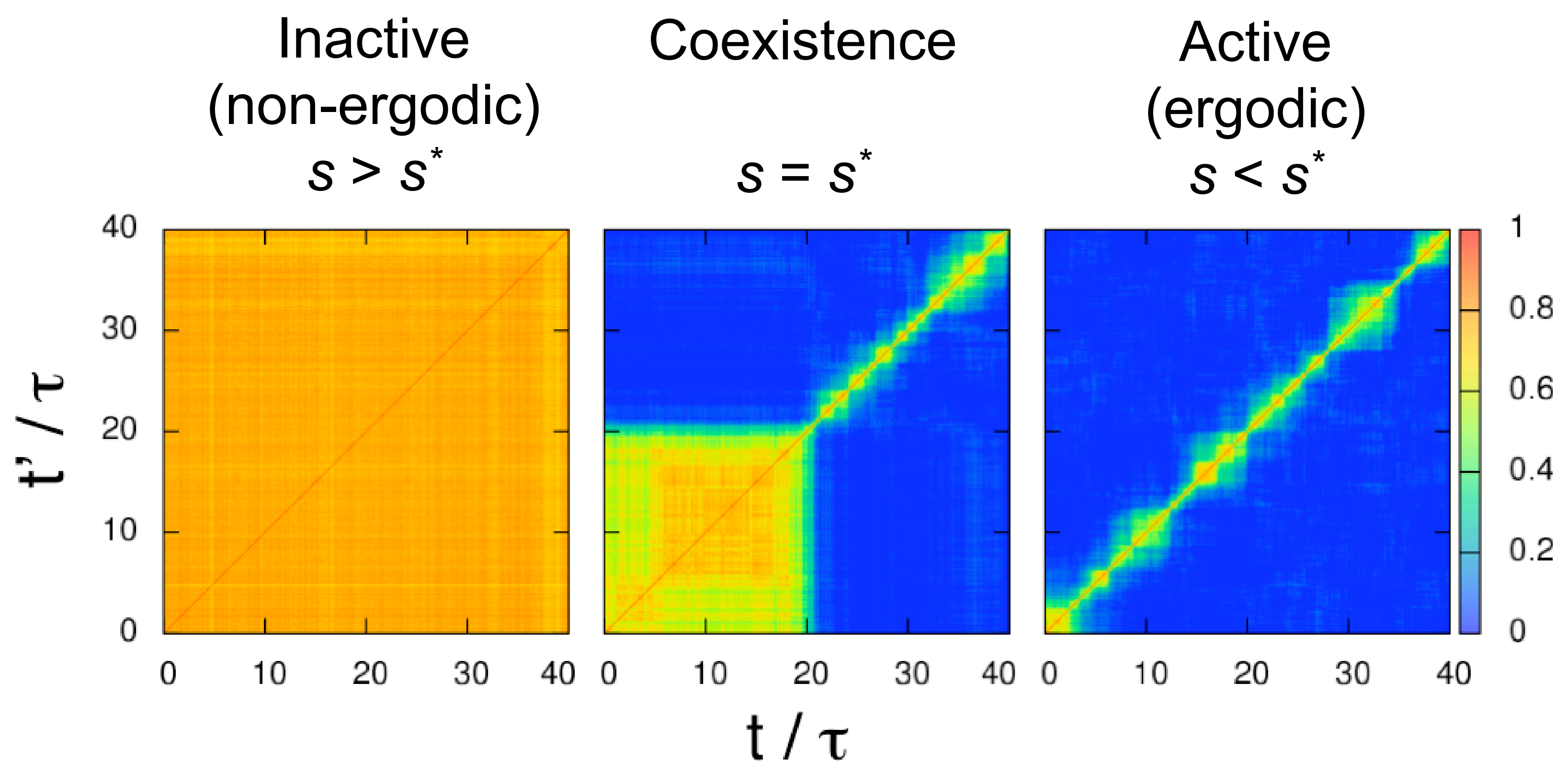
Overlap: $$Q(t,t') = N^{-1}\sum_{i=1}^{N}\cos\left\{\mathbf{q}\bullet\left[\mathbf{r}_i(t) - \mathbf{r}_i(t')\right]\right\}$$



Active-Inactive Coexistence, con'd

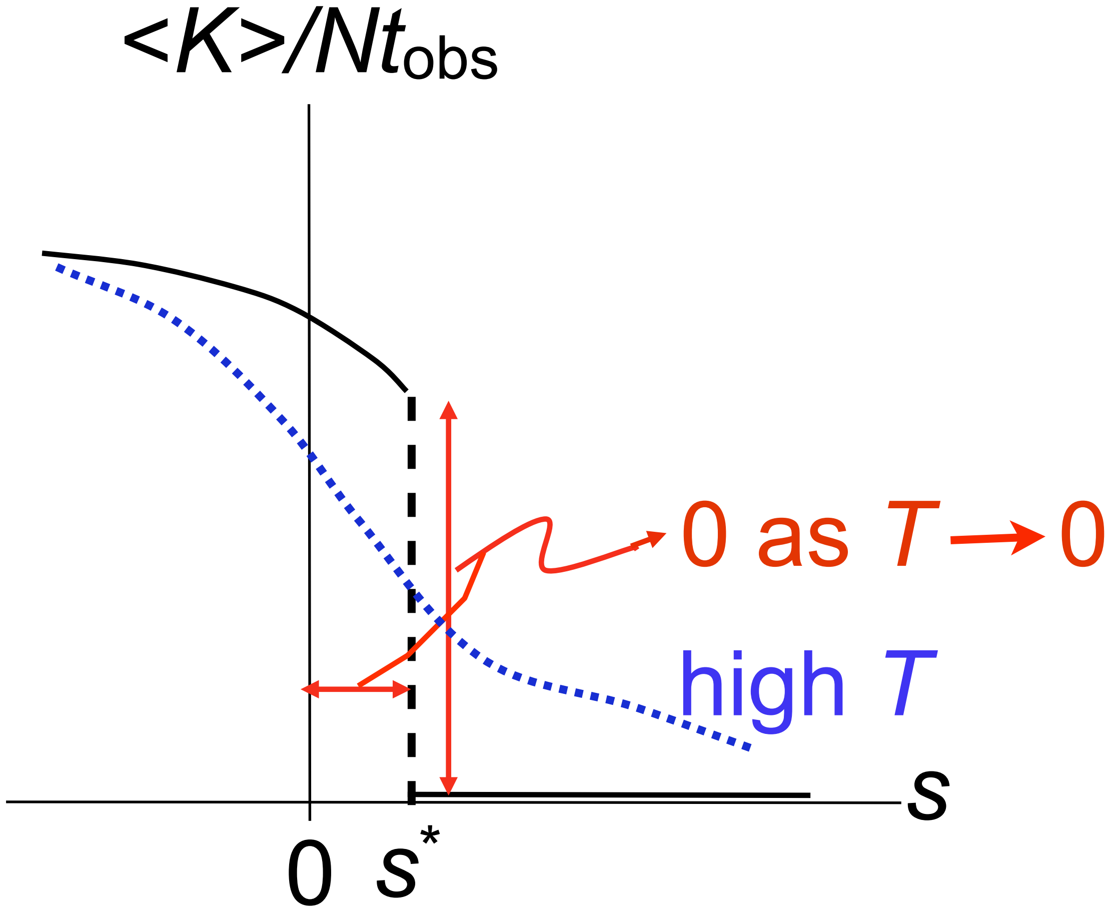
Hedges et al.
Science (2009)

Overlap: $$Q(t,t') = N^{-1} \sum_{i=1}^{N} \cos\left\{ \mathbf{q} \cdot \left[\mathbf{r}_i(t) - \mathbf{r}_i(t') \right] \right\}$$



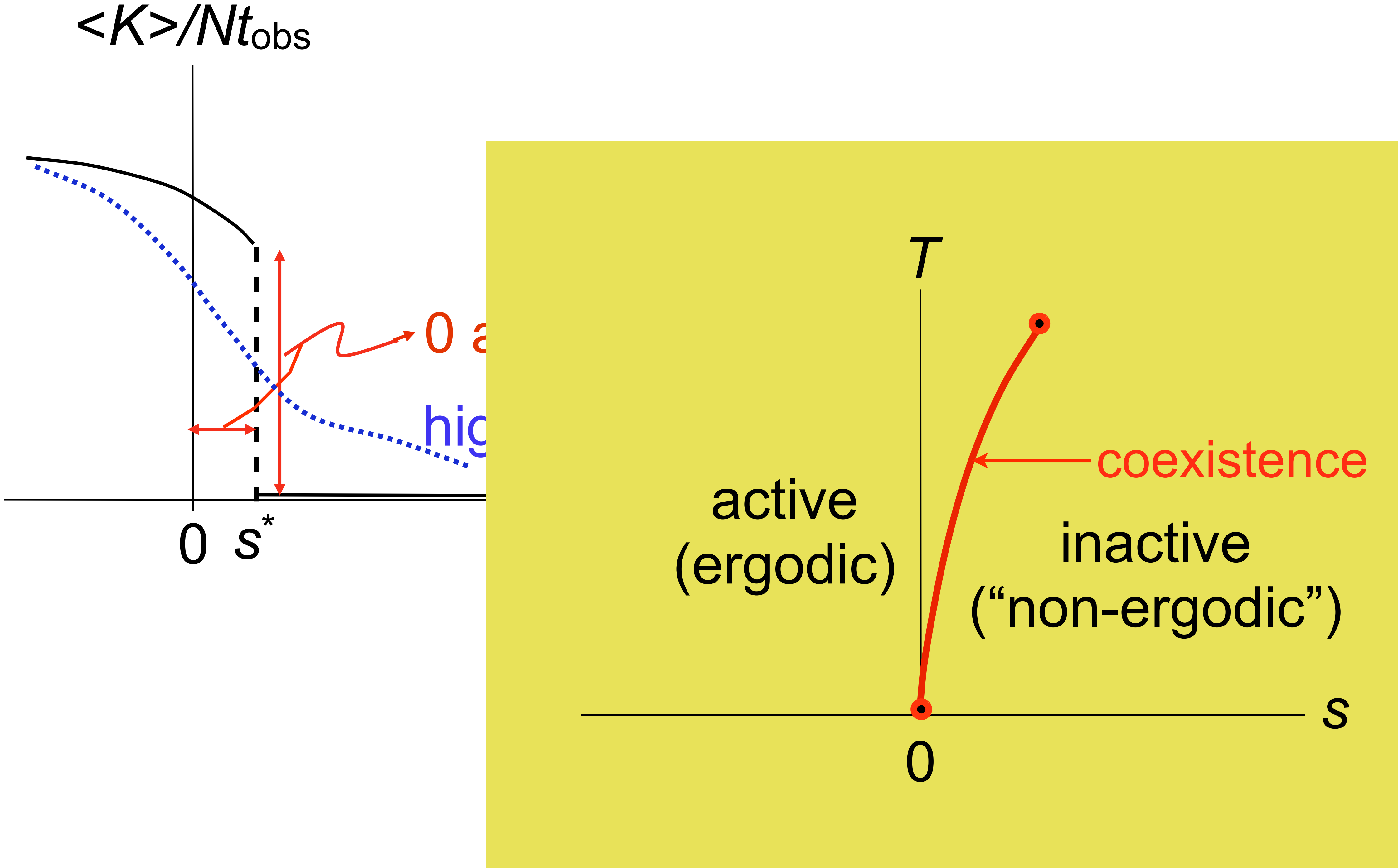
Sharp interface at coexistence

Phase diagram



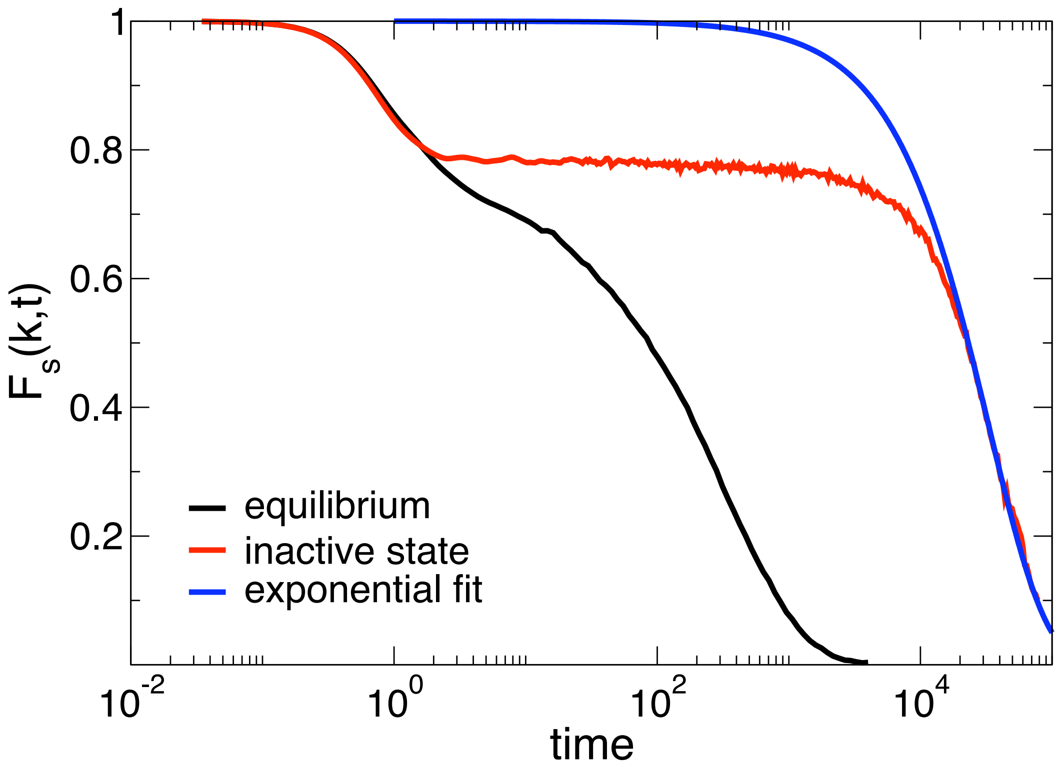
Garrahan, Jack, Lecomte, Pitard, Van Duijvendijk, Van Wijland , Phys. Rev. Lett.98, 195702 (2007) & J. Phys. A 42 075007 (2009); Elmatad, Jack, Garrahan & Chandler, arXiv:1002.3161 (2010)

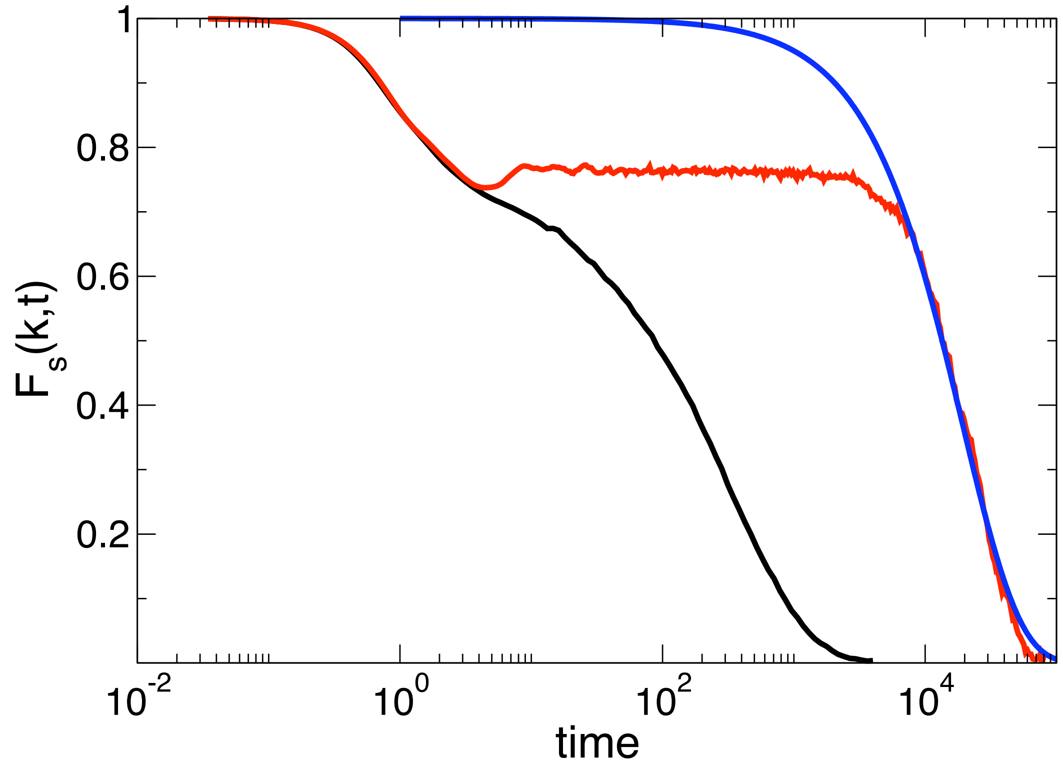
Phase diagram

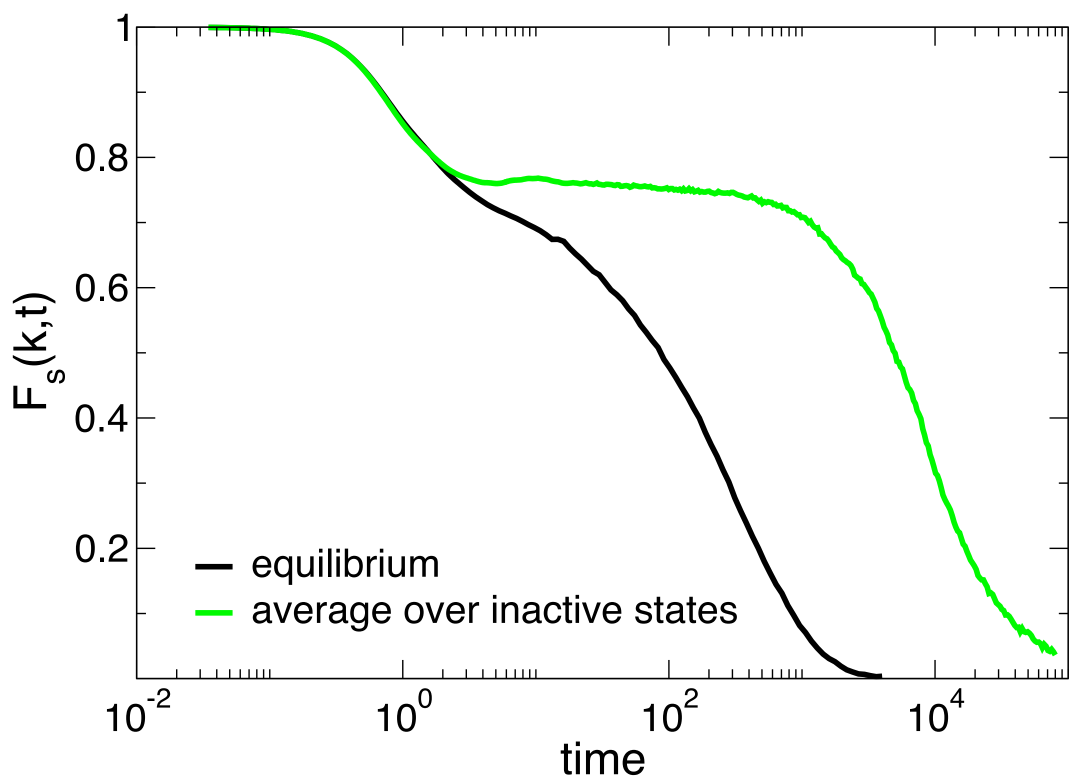


Garrahan, Jack, Lecomte, Pitard, Van Duijvendijk, Van Wijland , Phys. Rev. Lett.98, 195702 (2007) & J. Phys. A 42 075007 (2009); Elmatad, Jack, Garrahan & Chandler, arXiv:1002.3161 (2010)

Decay from inactive states. d=3 KA model, T=0.6 (T_o=0.7)



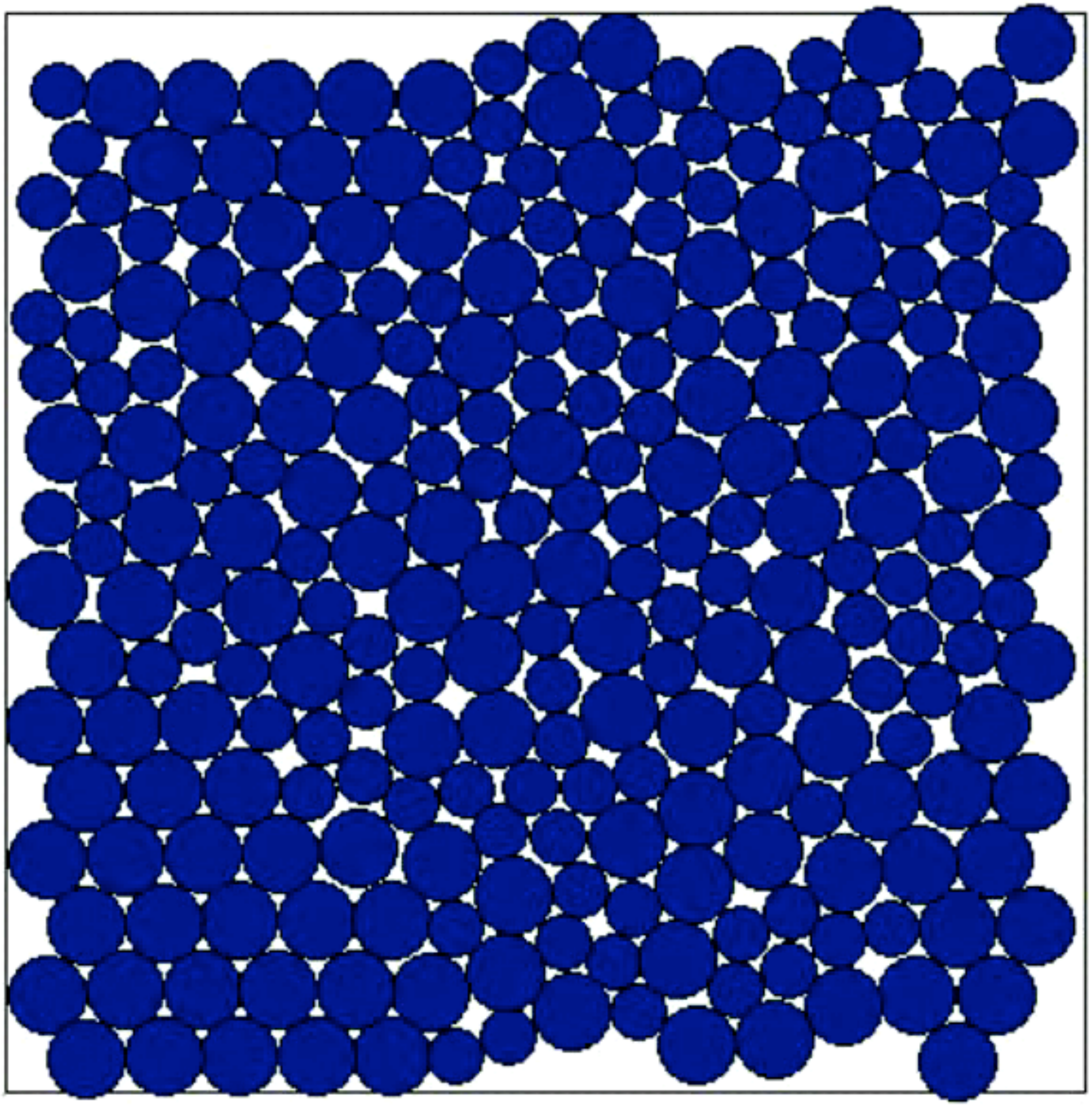




Decay from inactive states. d=2 WCA mixture, at T=1.0 (T_o = 1.5)

Movie runs for ~ $100\tau_\alpha$

Decay from inactive states. d=2 WCA mixture, at T=1.0 (T_o = 1.5)



Movie runs for ~ $100\tau_\alpha$