Connecting real glasses to mean field models

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Funding

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Transition Temperatures in Supercooled liquids

[Angell J. Res. Natl. Inst. Stand. Technol. 102, 171 (1997)]

Kauzmann Temperature
Relaxation time → diverges
Configurational Entropy → vanishes

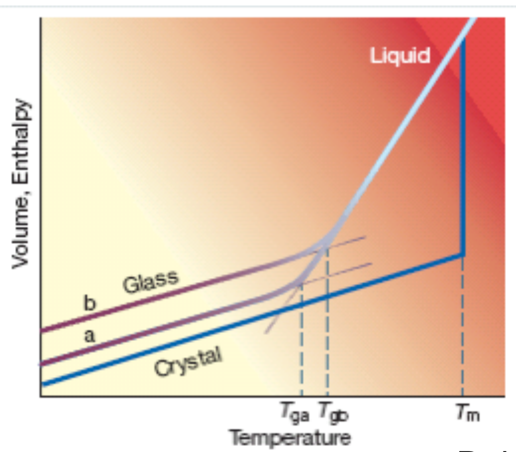
Mode Coupling theory transition temperature
Relaxation time → Avoided Power law divergence

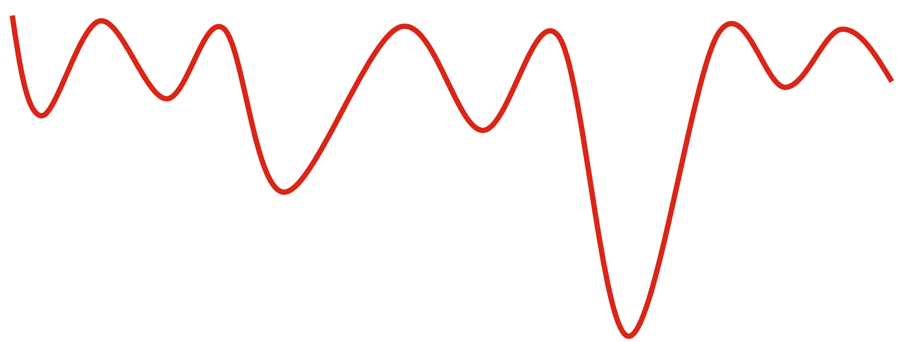
T_{VFT}/ T_K T_C T

T_g T_{Onset}

Laboratory glass transition
Viscosity= 10^{13} poise
Relaxation time=100 sec

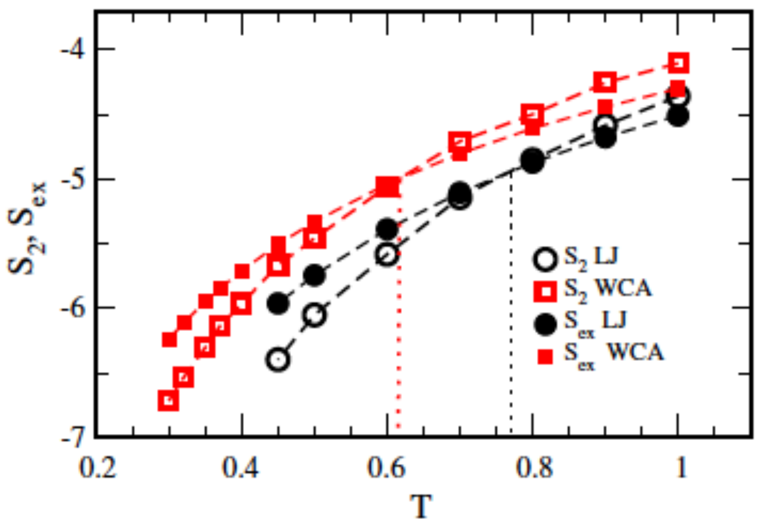
Dynamic Heterogeneity
Stokes-Einstein Breakdown
Landscape influenced dynamics
Activated dynamics





Debenedetti & Stillenger Nature, 410, 259 (2001)

Entropy and Transition temperatures

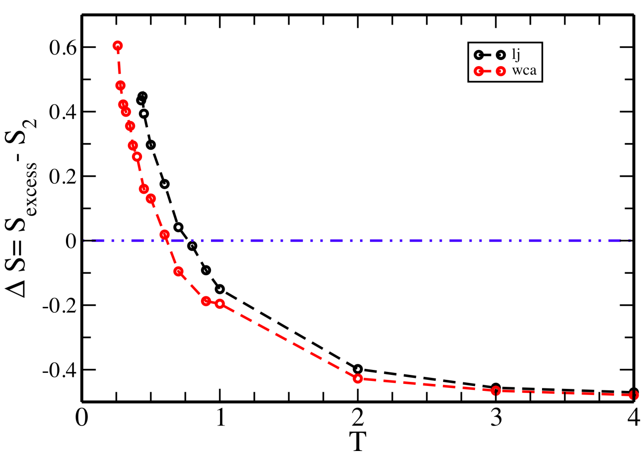


Excess entropy

$$S_{ex} = S_{total} - S_{id} = S_2 + \Delta S$$

Pair excess entropy

$$S_2 / k_B = -\frac{\rho}{2} \sum_{\alpha\beta} x_\alpha x_\beta \int d^3 r \left[g_{\alpha\beta}(r) \ln\left[g_{\alpha\beta}(r) \right] - g_{\alpha\beta}(r) + 1 \right]$$



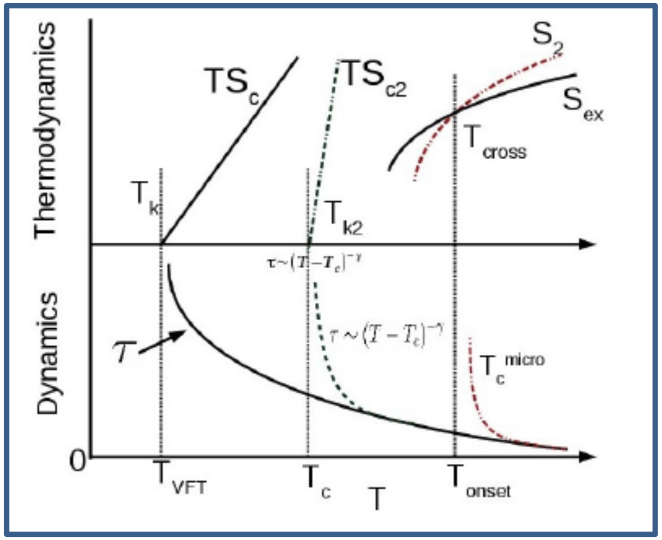
$\Delta S = 0$ Onset

$\Delta S > 0$ Activated motion

	$\rho = 1.2$		$\rho = 1.4$		$\rho = 1.6$			
	LJ	WCA	LJ	WCA	LJ	WCA	WAHN	NTW
$T_{Plateau-arises}$	0.9-0.8	0.7-0.6	1.7-1.6	1.6-1.4	3.25-2.75	3.25-2.75	1.0-0.9	0.51-0.44
$T_{eIS-drop}$	0.9-0.78	0.7-0.6	1.6-1.5	1.5-1.4	2.80-2.85	2.8-3.75	0.8-0.75	0.55-0.5
$T^{SE}_{breakdown}$	0.781	0.609	1.57	1.43	2.782	2.707	0.8	0.492
$T_{crossing}$	0.77	0.61	1.50	1.43	2.86	2.85	0.86	0.58

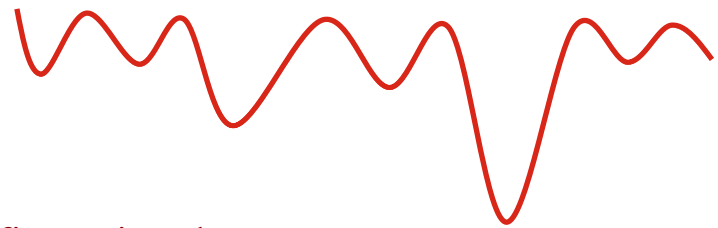
Banerjee, Nandi, Sastry, and Bhattacharyya, J. Chem. Phys. **147** 024504 (2017).

Entropy and Transition temperatures



Configurational entropy $S_c = S_{ideal} + S_{ex} - S_{vib}$

Count of minima



Pair configurational entropy

$$S_{c2} = S_{ideal} + S_2 - S_{vib}$$

	LJ			WCA			WAHN	NTW
	$\rho = 1.2$	$\rho = 1.4$	$\rho = 1.6$	$\rho = 1.2$	$\rho = 1.4$	$\rho = 1.6$	$\rho = 1.296$	$\rho = 1.655$
T_c	0.435	0.93	1.76	0.28	0.81	1.69	0.55	0.31
T_{K2}	0.445	0.929	1.757	0.268	0.788	1.696	0.544	0.34

Nandi, Banerjee, Dasgupta, Bhattacharyya **PRL**, **119** 265502 (2017)

Banerjee, Sengupta, Sastry and Bhattacharyya **PRL** **113**, 225701 (2014)

- Configurational entropy → Activated dynamics
- MCT → mean field theory no activation

?????

Molecular mean field theory

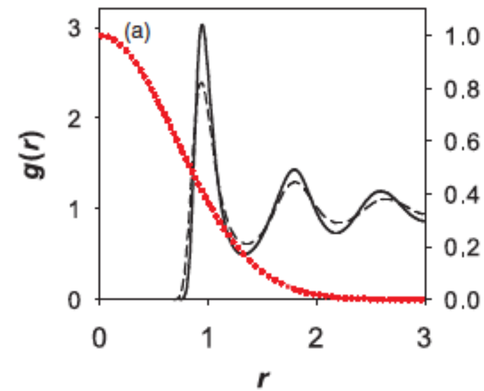
Information of MCT transition temperature embedded in the pair correlation function g(r)/S(q)

M. Nandi, A. Banerjee, C. Dasgupta, S. M. Bhattacharyya **PRL**, 265502 (2017)

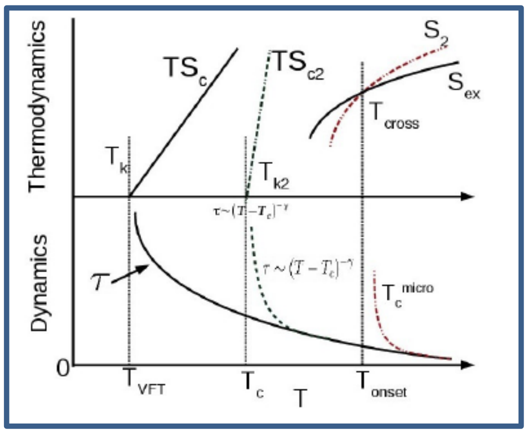
Entropy and Transition temperatures for Mean field models

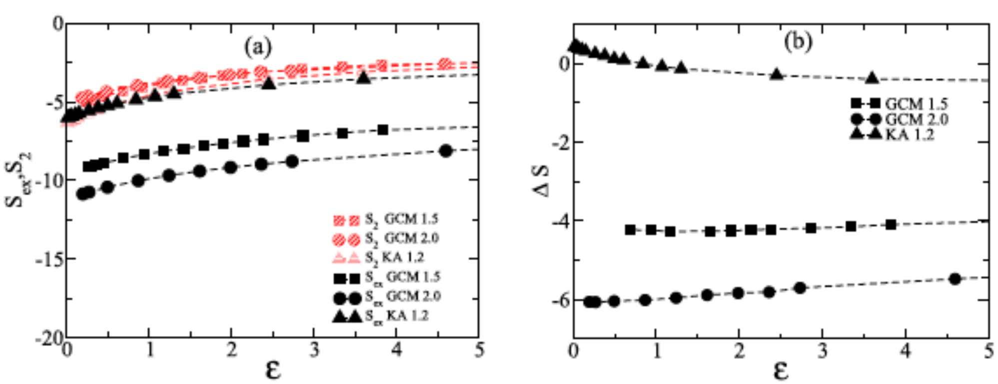
Gaussian Core Model — Mean field model

$$U(r) = \epsilon_o exp[-(r/\sigma)^2]$$



Can we predict transition temperatures from entropy ??





- No crossing between S_2 and S_{ex}
- High and low temperatures - large many body contribution
- No correlation between MCT transitio temperature and pair entropy

Nandi and Bhattacharyya J. Chem. Phys. **148**, 034504 (2018).

Development of Mean field Model

3D $\longrightarrow$ mean field

Parameter

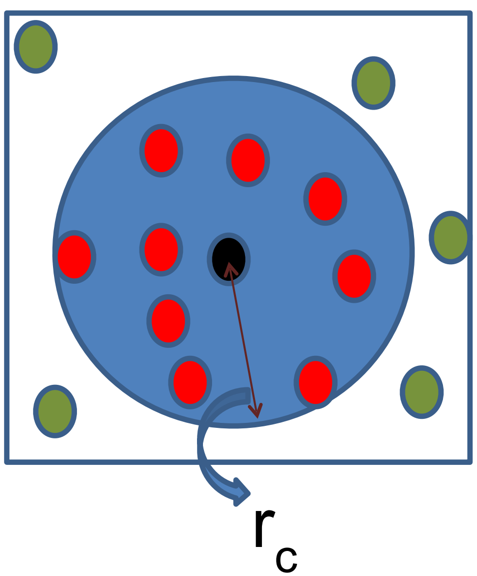
- Range of the potential (GCM / Mari & Kurchan Model , JCP, 135, 124504 (2011)
- Dimension of the system
- **Assign Pseudo neighbours to each particle**

$$u = u_{direct} + u_{pseudo}$$

$$u^{ij}_{direct} = 4\epsilon\Big[\Big(\frac{\sigma_{ij}}{r_{ij}}\Big)^{12} - \Big(\frac{\sigma_{ij}}{r_{ij}}\Big)^{6}\Big]$$

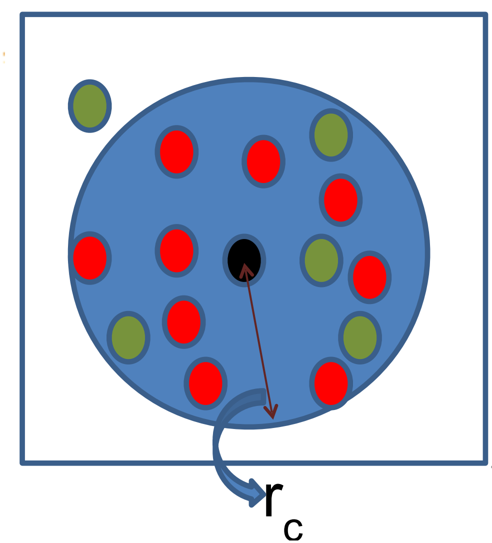
$$u^{ij}_{pseudo} = 4\epsilon\Big[\Big(\frac{\sigma_{ij}}{r_{ij} - L_{ij}}\Big)^{12} - \Big(\frac{\sigma_{ij}}{r_{ij} - L_{ij}}\Big)^{6}\Big]$$

Normal system

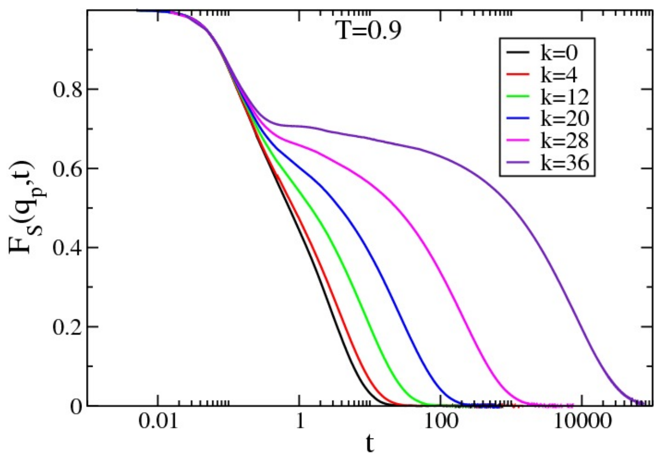


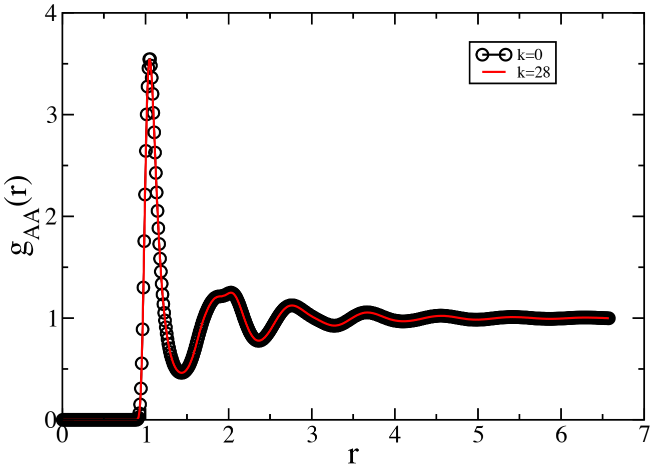
r_{ij}-L_{ij}

Addition of Pseudo neighbours



Structure and Dynamics as function of 'k'

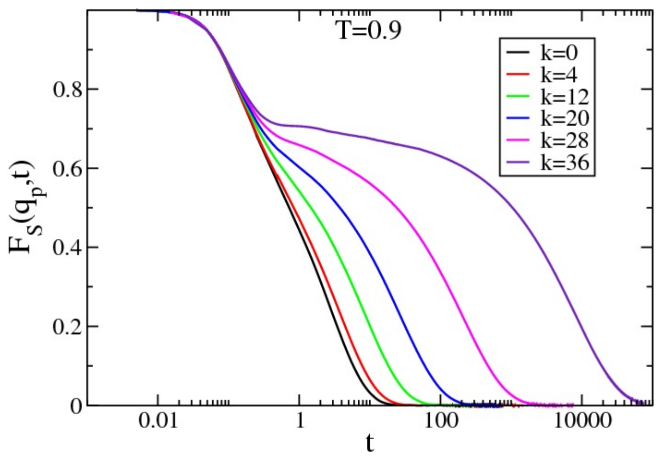


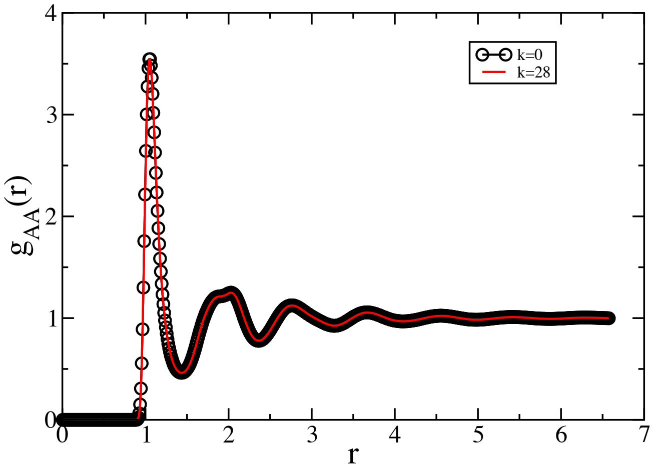


Structure remains same but dynamics changes over orders of magnitude

Ujjwal Nandi, Kob and Bhattacharyya, Ms. under preparation

Structure and Dynamics as function of 'k'





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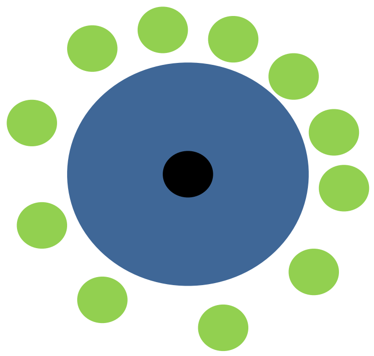

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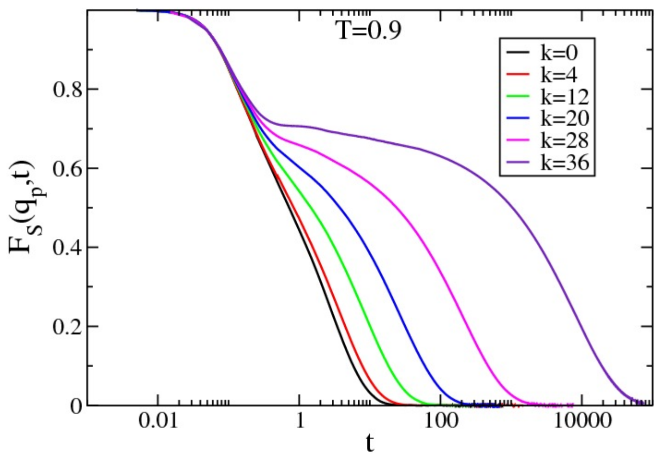
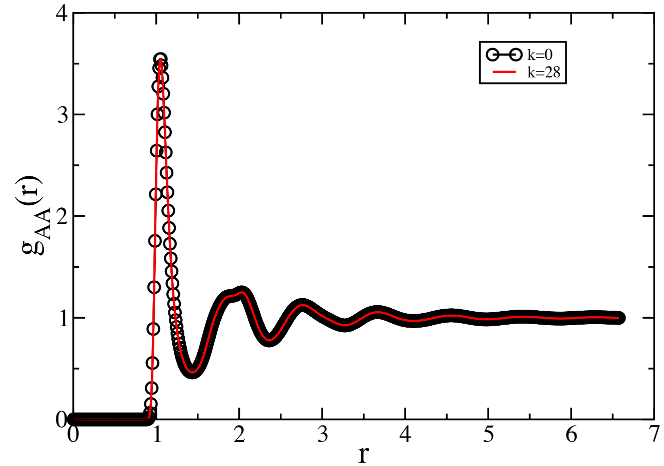
Structure and Dynamics as function of 'k'





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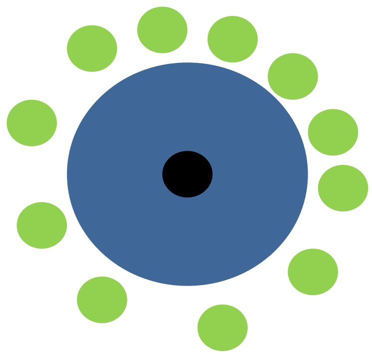

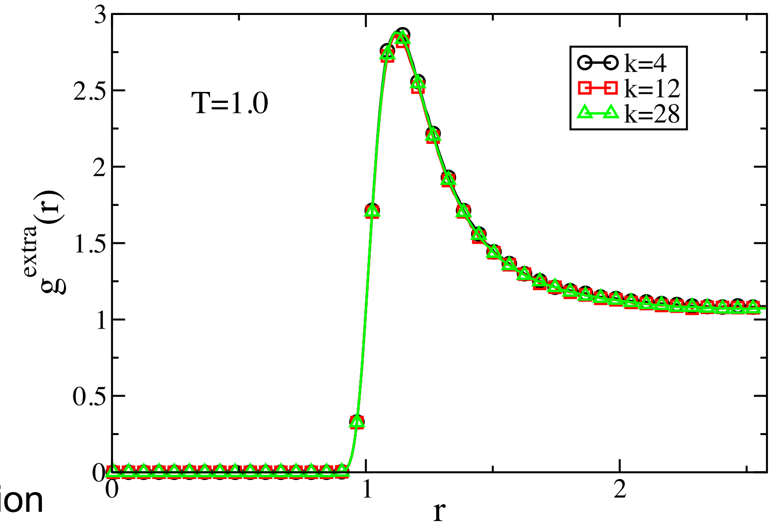

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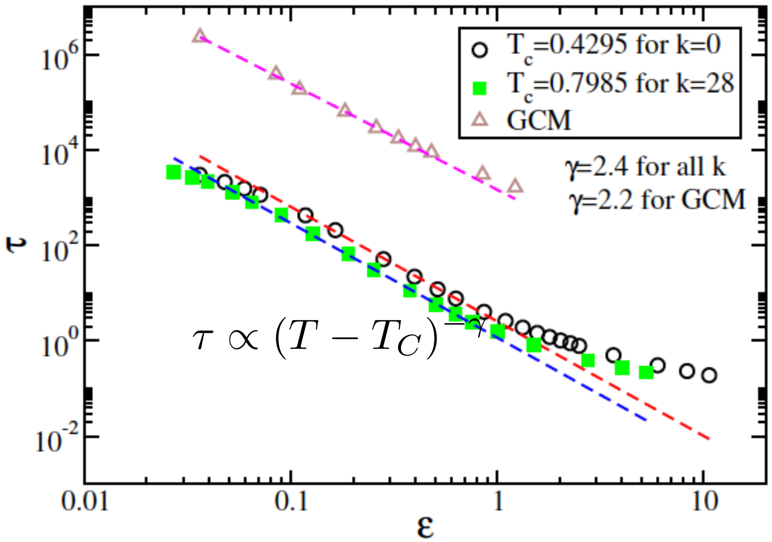
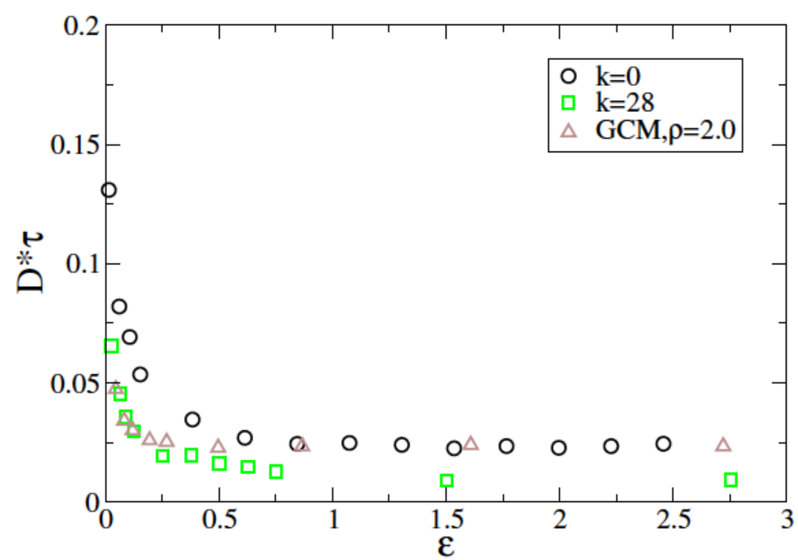
Test of mean field behaviour

MCT Power Law Behaviour



MCT Follows till a lower temperature
—> Mean field

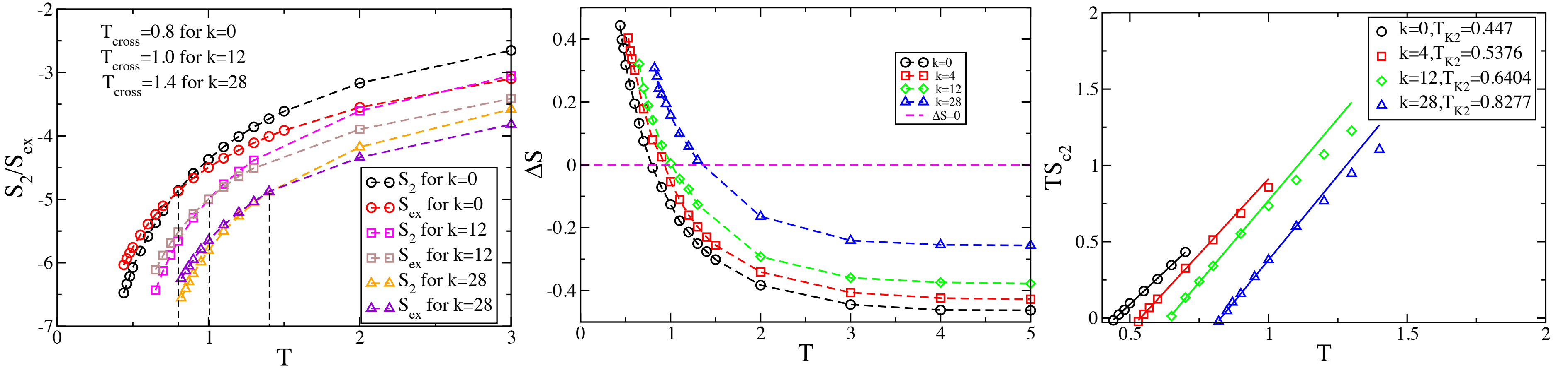
Stokes Einstein Decoupling



Less degree of SE decoupling —> Mean Field

$$\epsilon = (T - T_c)/T_c$$

Transition temperatures from Entropy



	k=0	k=4	k=12	k=28
T_{onset}	0.75	0.92	1.06	1.38
$T_{crossing}$	0.8	0.925	1.0	1.4
T_{K2}	0.447	0.5376	0.6404	0.8277
T_C	0.4338	0.5086	0.6234	0.799

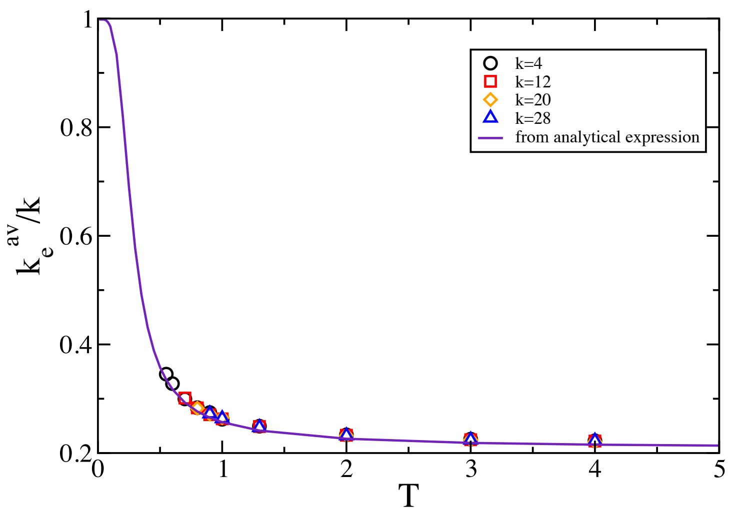
With increase in 'k' more contribution from pair

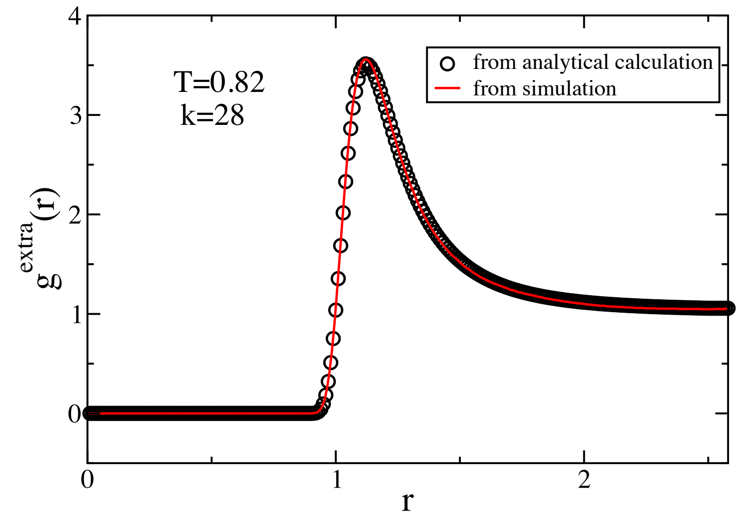
Ujjwal Nandi, Kob and Bhattacharyya, Ms. under preparation

Pseudo Neighbour Statistics

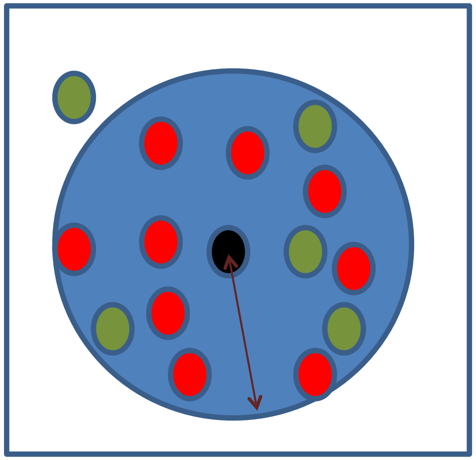
Probability of pseudo neighbours

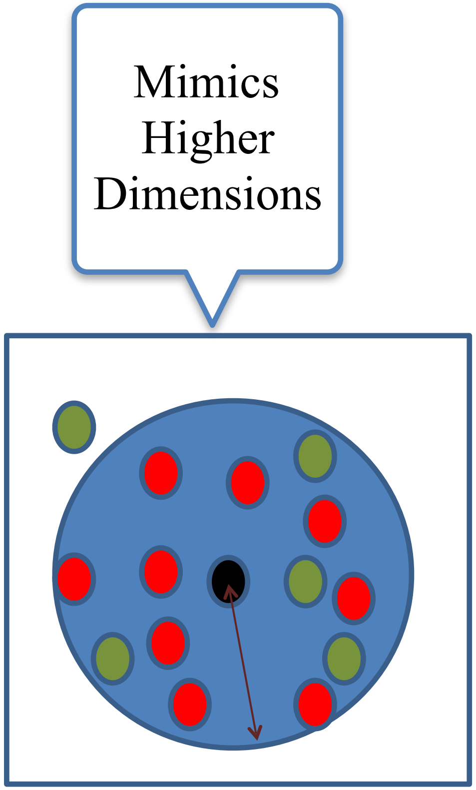
$$P = \frac{k_e^{av}}{k} = \frac{\int_{V\,acc} d\mathbf{r}\ exp(-\beta u_{pseudo}(r)Y(r))}{\int_{V\,acc} d\mathbf{r}\ exp(-\beta u_{pseudo}(r))}$$

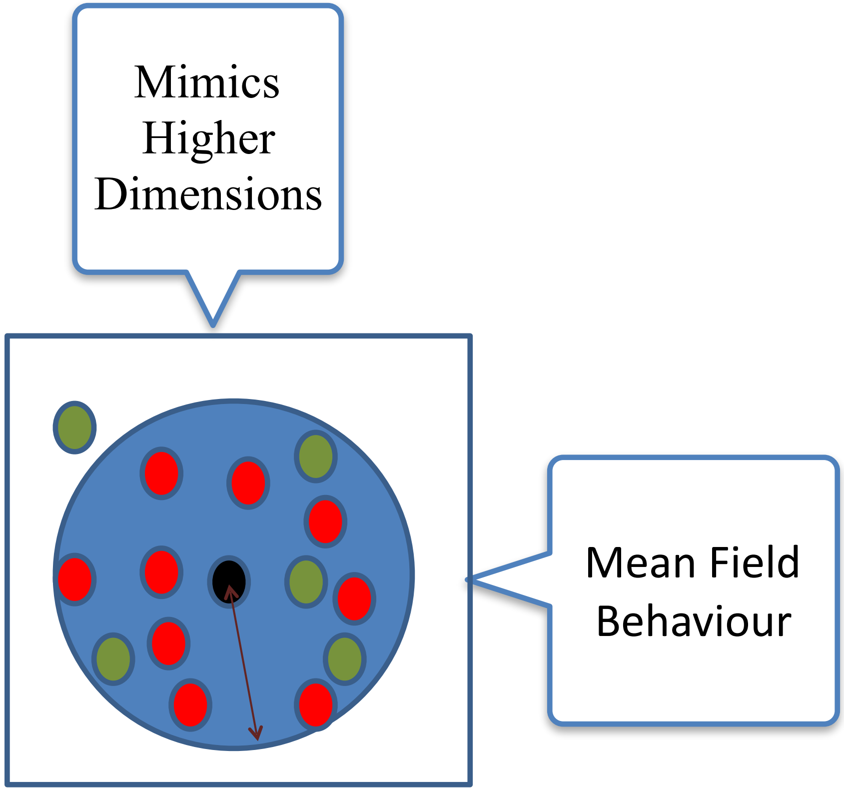


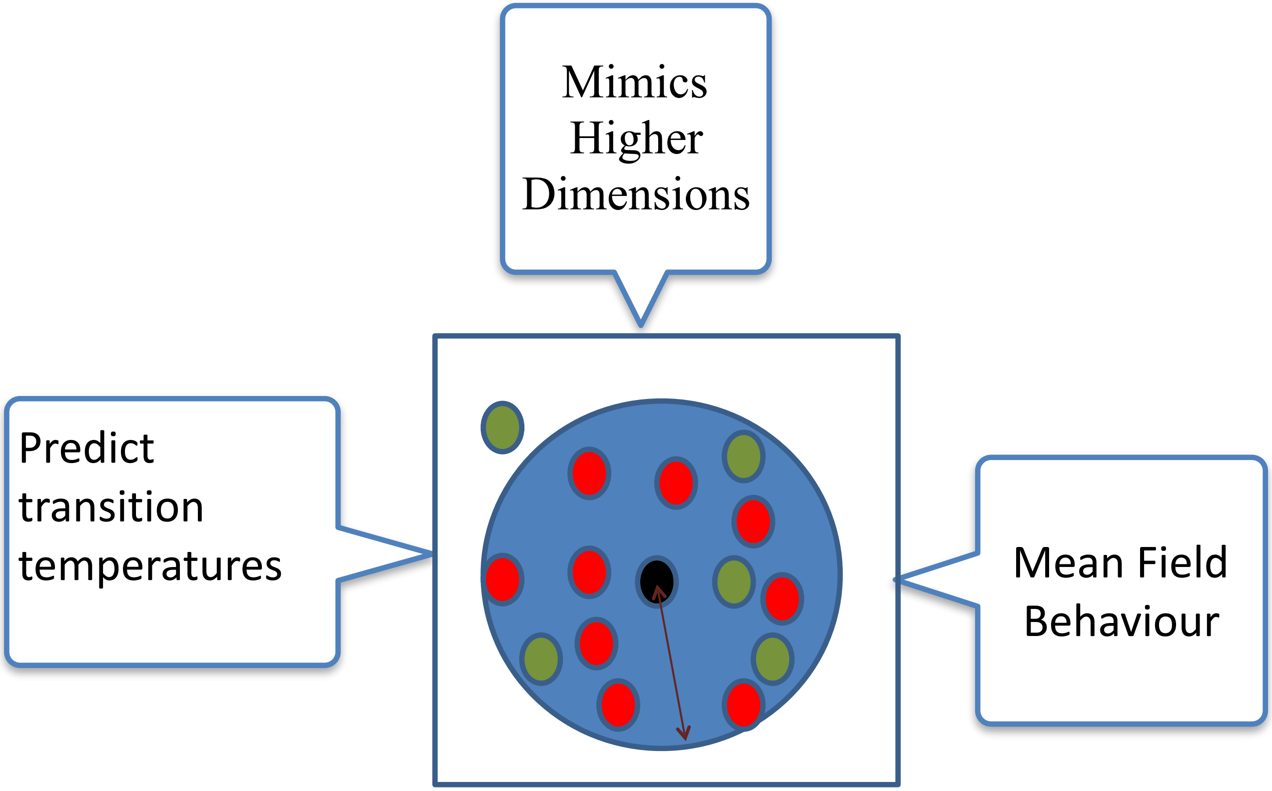


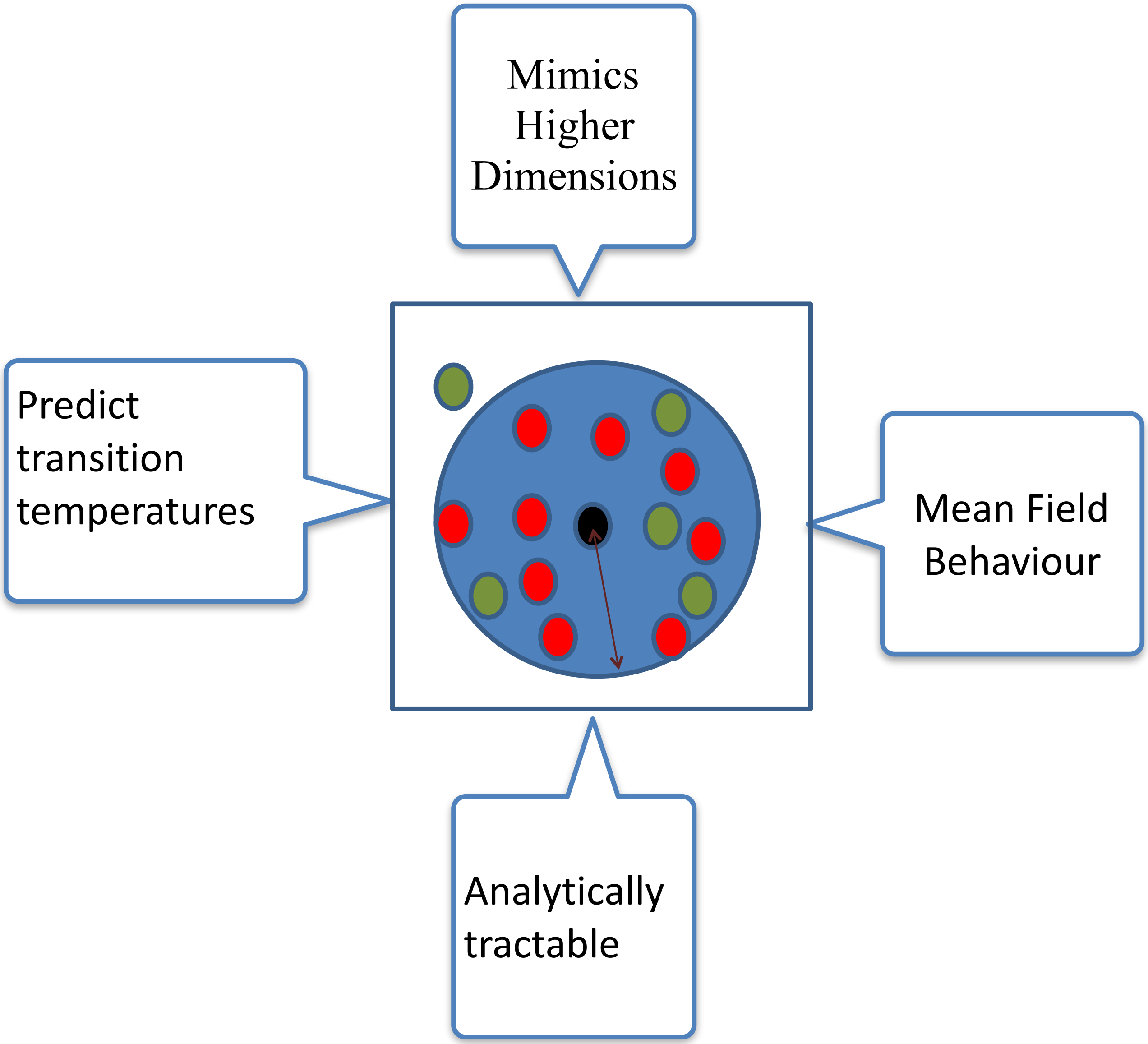
- Master plots of pseudo neighbour statistics
- Analytically tractable




Mimics
Higher
Dimensions


Mimics Higher Dimensions
Mean Field Behaviour


Mimics Higher Dimensions
Predict transition temperatures
Mean Field Behaviour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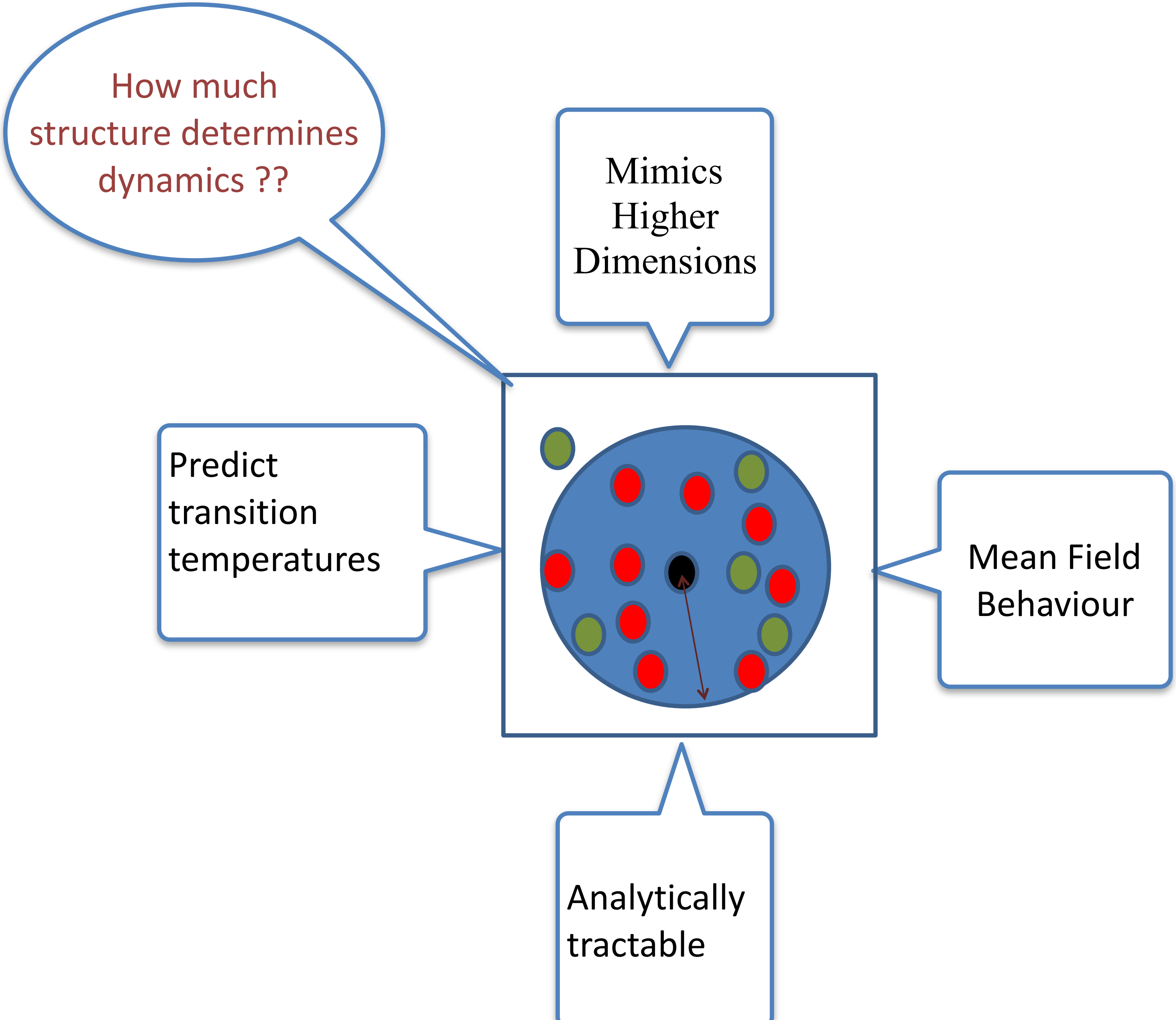
How much structure determines dynamics ??
Mimics Higher Dimensions
Predict transition temperatures
Mean Field Behaviour
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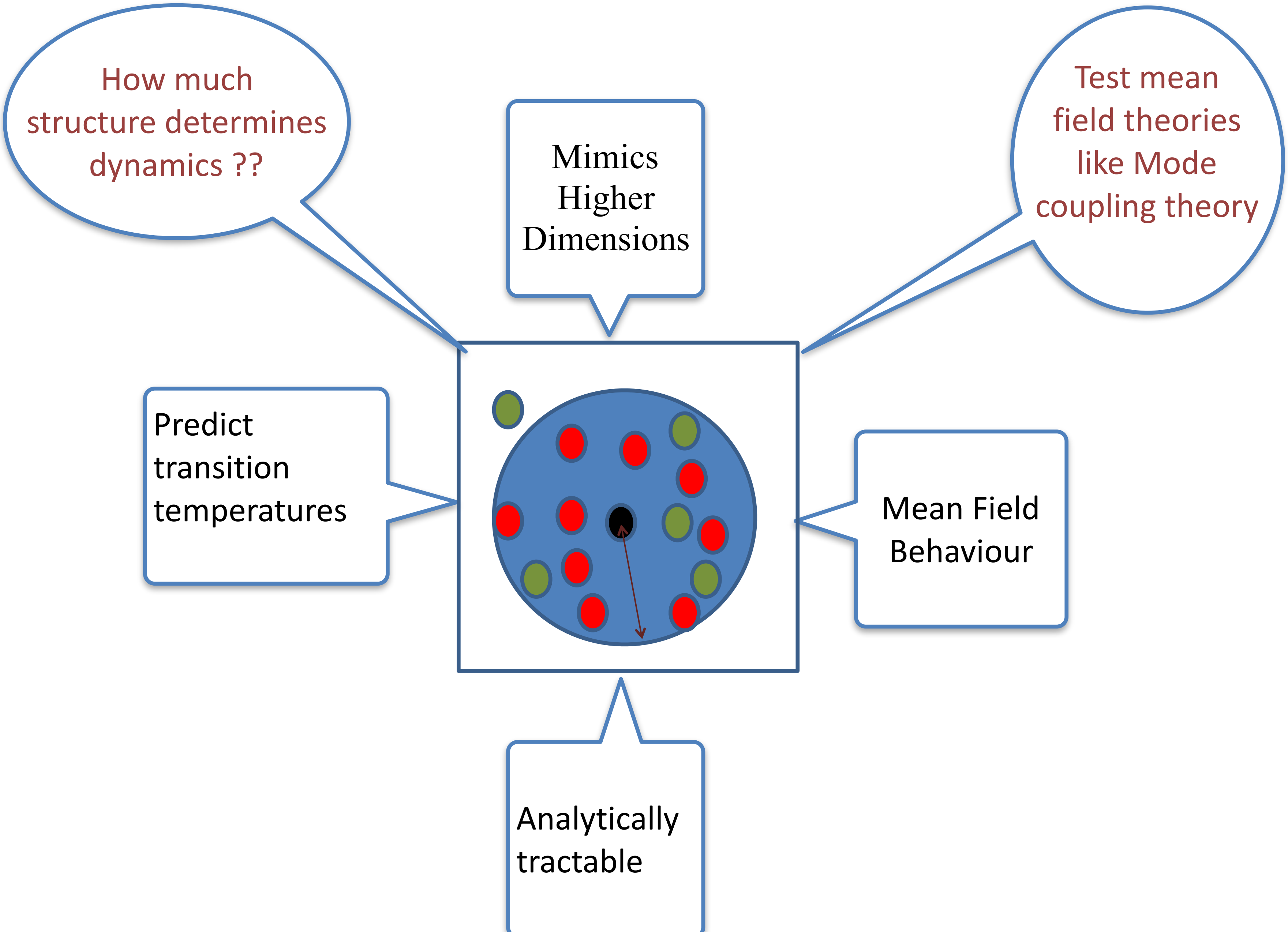
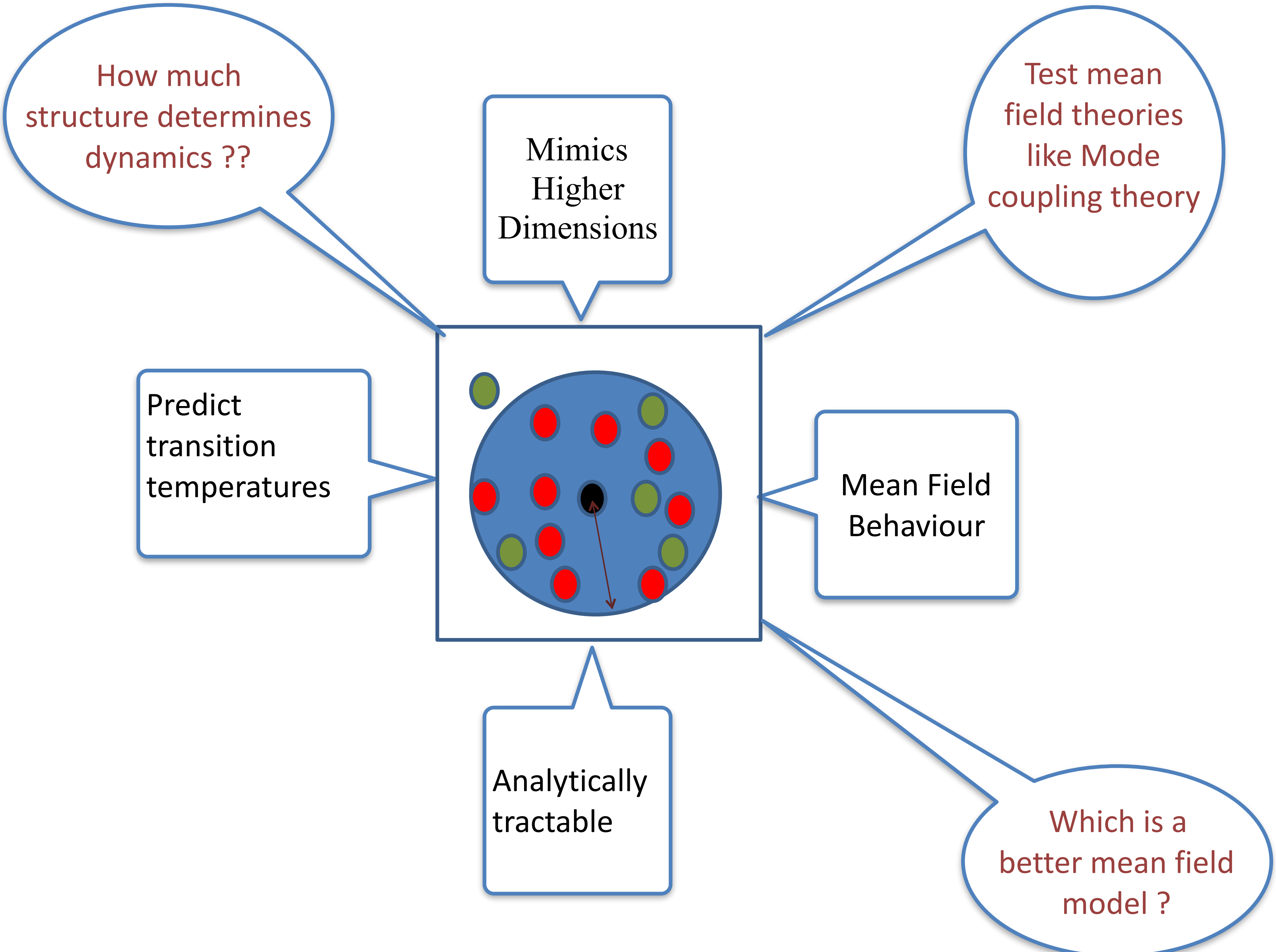
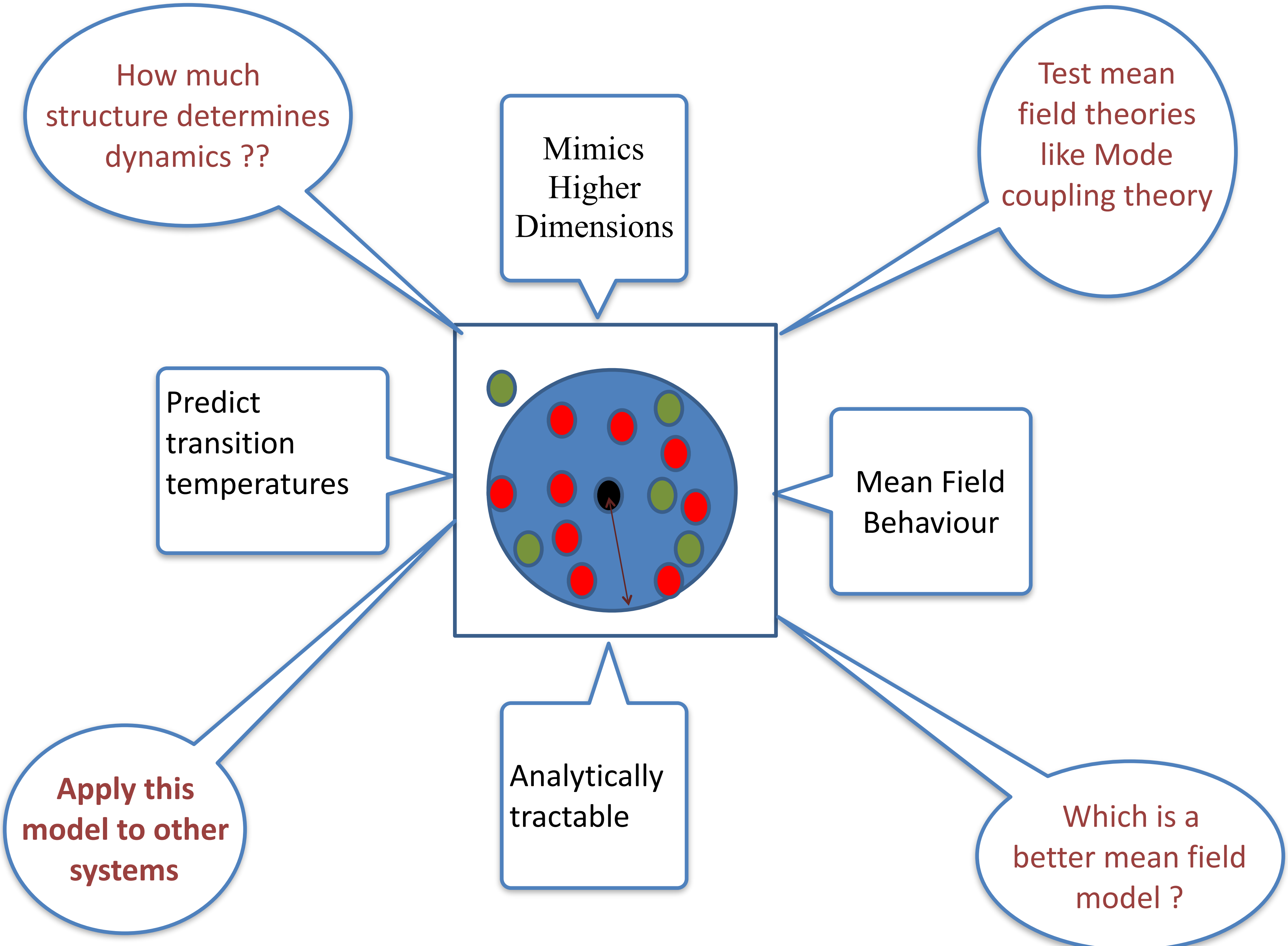

How much structure determines dynamics ??
Mimics Higher Dimensions
Test mean field theories like Mode coupling theory
Predict transition temperatures
Mean Field Behaviour
Analytically tractable


How much structure determines dynamics ??
Mimics Higher Dimensions
Test mean field theories like Mode coupling theory
Predict transition temperatures
Mean Field Behaviour
Analytically tractable
Which is a better mean field model ?


How much structure determines dynamics ??
Mimics Higher Dimensions
Test mean field theories like Mode coupling theory
Predict transition temperatures
Mean Field Behaviour
Apply this model to other systems
Analytically tractable
Which is a better mean field model ?

Thank you for your attention !!