The role of pair correlation function in the dynamical transition predicted by the mode coupling theory

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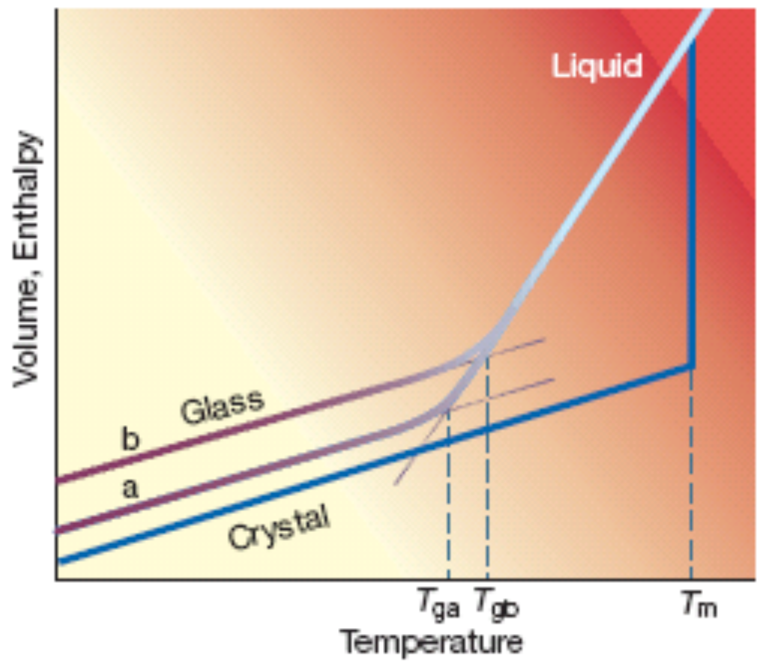
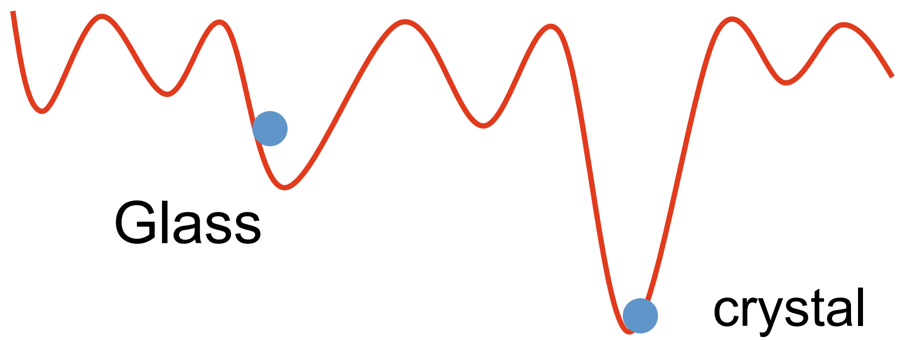
Supercooled liquid and glass transition

- Fast cooling → Nucleation suppressed → Below T_m supercooled liquid
- Supercooled Liquid on cooling → Amorphous solid (glass) at T_g



Debenedetti & Stillenger Nature, 410, 259 (2001)



Transition Temperatures

Kauzmann Temperature
Relaxation time → diverges
Configurational Entropy → vanishes

MCT transition temperature
Relaxation time → Avoided Power law divergence

T_K T_g T_C T_{Onset} T

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

Dynamic Heterogeneity
Stokes-Einstein Breakdown
Landscape influenced dynamics
Activated dynamics

Broad outline

- Mode coupling theory → its success and failure
- From Structure to dynamics via entropy
- Molecular mean field theory

Mode coupling theory (MCT)

Pair Structure g(r)/S(q) → MCT → Dynamics

$$\ddot{F}(k,t) + \gamma \dot{F}(k,t) + \Omega_k^2 F(k,t) + \Omega_k^2 \int M(k,t-t')\,\dot{F}(k,t')\,dt' = 0$$

- $\ddot{F}(k,t)$ → Force term
- $\gamma \dot{F}(k,t)$ → Damping term
- $\Omega_k^2 F(k,t)$ → potential
- $M(k,t-t')$ → Memory kernal

$$M(k,t) = \frac{\rho S(k)}{2k^2} \int \frac{d\vec{q}}{(2\pi)^3} V_k^2(\vec{q},\vec{k}-\vec{q}) S(k-q) S(q) F(|\vec{k}-\vec{q}|,t) F(q,t)$$

Vertex →

$$V_k^2(\vec{q},\vec{k}-\vec{q}) = \hat{k}.\vec{q}\,C(q) + \hat{k}.(\vec{k}-\vec{q})\,C(|\vec{k}-\vec{q})$$

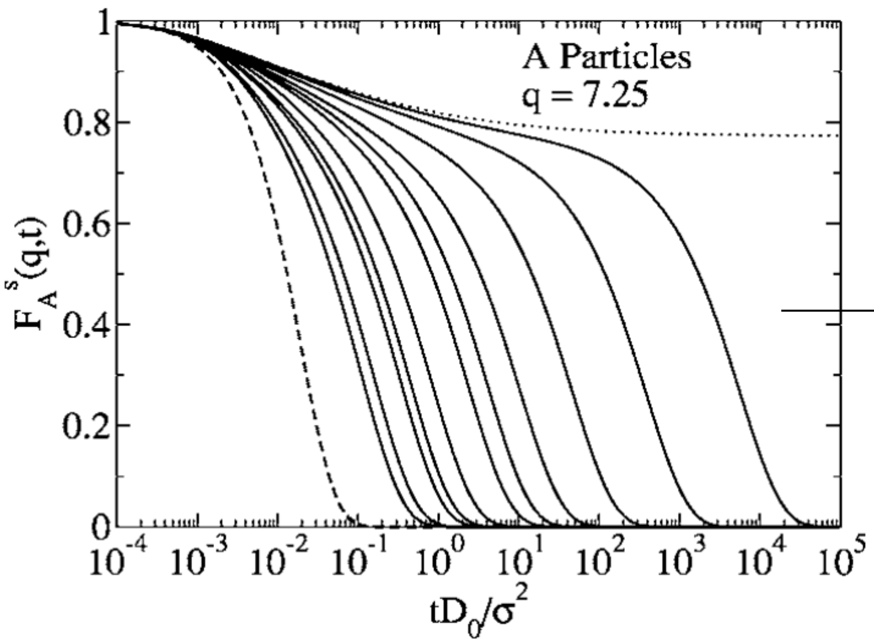
$$F(z) = \frac{1}{z - \frac{<\Omega_k^2>}{z+M(z)}} \qquad M(z) = i\gamma + 4\lambda <\Omega_k^2> \mathcal{L}\{F^2(t)\}$$

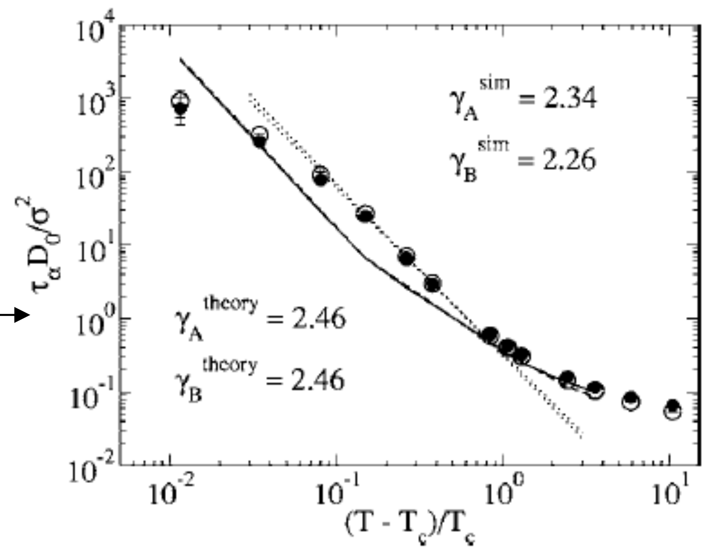
Mode coupling theory predictions

MCT predicts $\longrightarrow$ $$\tau_\alpha \propto \left(T - T_C\right)^{-\gamma}$$

S(q) → Microscopic MCT → Divergence of relaxation time

$$\ddot{F}(k,t) + \gamma \dot{F}(k,t) + \Omega_k^2 F(k,t) + \Omega_k^2 \int M(k,t-t')\dot{F}(k,t')\,dt' = 0$$



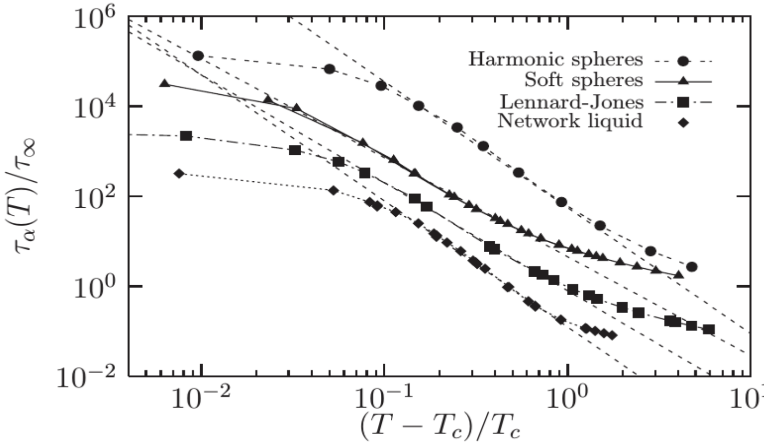


Gives T_c^{micro}

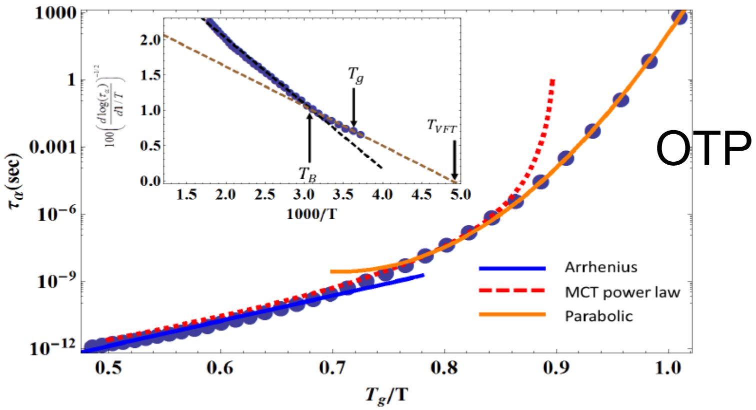
PRE 72, 031508 (2005)

MCT power law behaviour and T_c

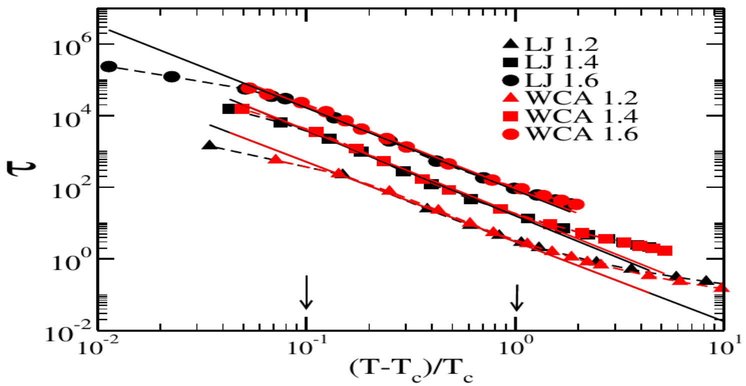
$$\tau \sim (T - T_c)^{-\gamma}$$



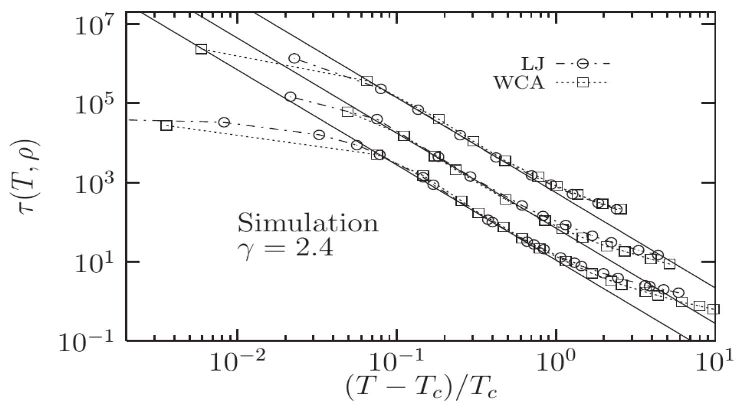
PRE 86,031502 (2012)



J. Phys. Chem. Lett., 4, 3648 (2013)



JCP 143, 174504 (2015)



PRE 82,031502 (2010)

Discrepancy between microscopic MCT (T_c^{micro}) and power law fit (T_c)

	$\rho = 1.2$	$\rho = 1.4$	$\rho = 1.6$
T_c^{micro} (LJ)	0.8971	1.8677	3.528
$T_c(LJ)$	0.435	0.93	1.76
T_c^{micro} (WCA)	0.7419	1.7707	3.489
$T_c(WCA)$	0.28	0.81	1.69

$T_c^{micro} > T_c$

Possible origin of discrepancy

- **Feedback mechanism**

Sensitive to small changes in S(q)

$$F(z) = \frac{1}{z - \frac{<\Omega_k^2>}{z+M(z)}}$$

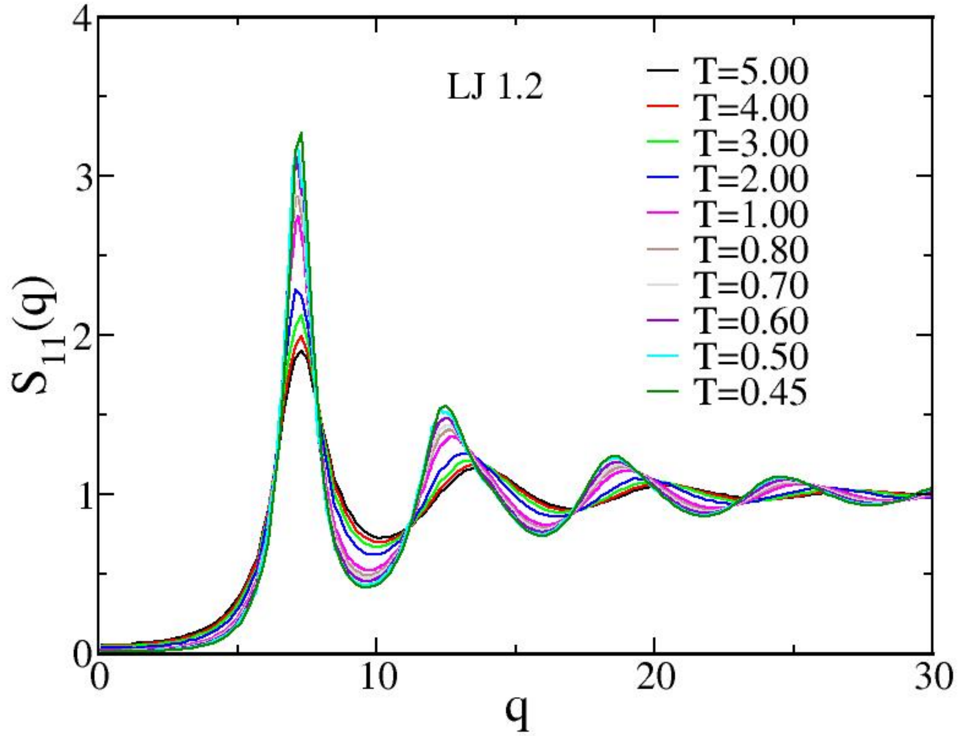
$$M(z) = i\gamma + 4\lambda < \Omega_k^2 > \mathcal{L}\{F^2(t)\}$$

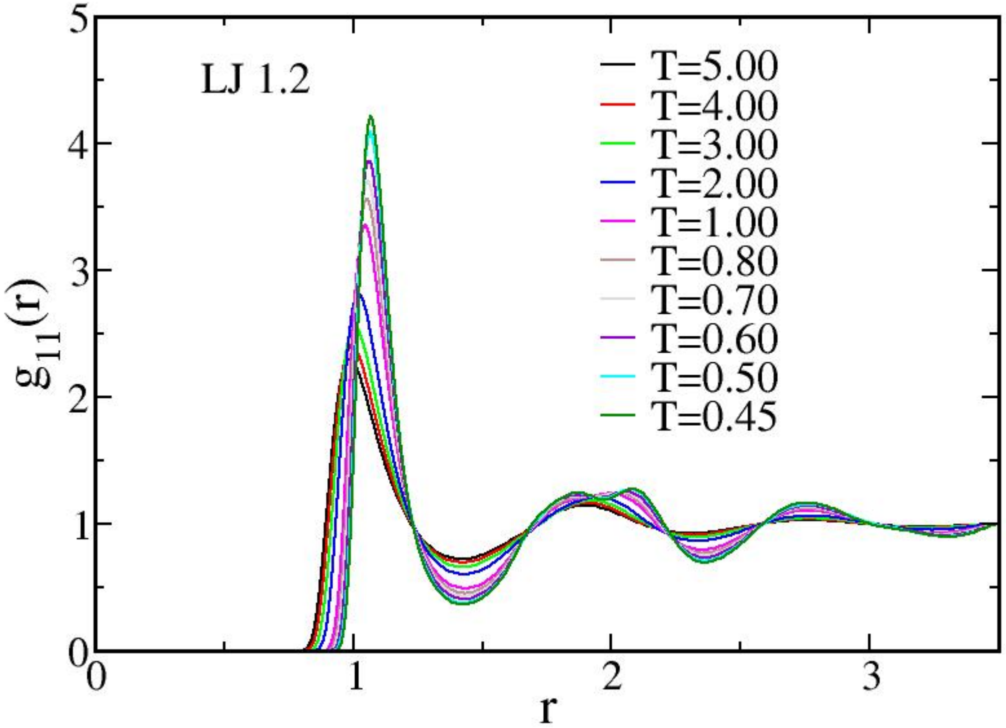
- Vertex (coupling constant) corrections are needed

$$V_k^2(\vec{q},\vec{k}-\vec{q}) = \hat{k}.\vec{q}C(q) + \hat{k}.(\vec{k}-\vec{q})C(|\vec{k}-\vec{q})$$

Nandi et al.J. Chem. Phys. 143, 174504 (2015)

Across the transition pair correlation appears benign

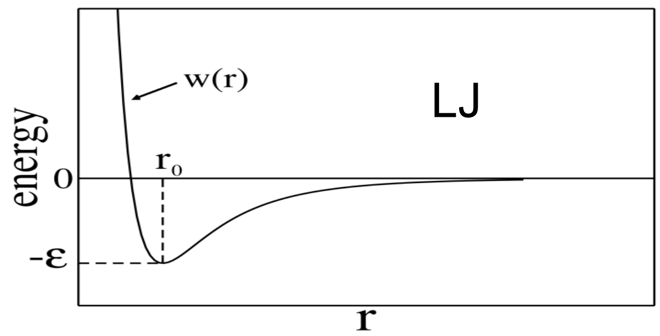


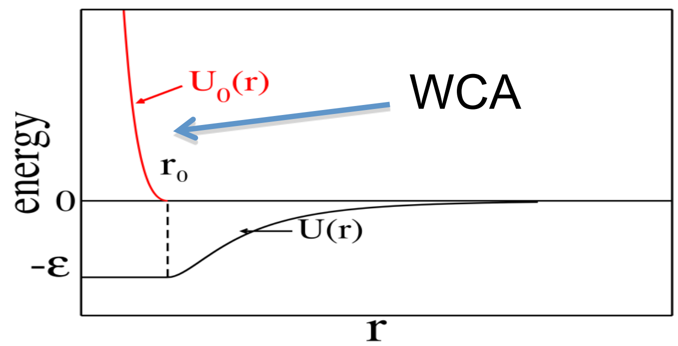


Broad Outline

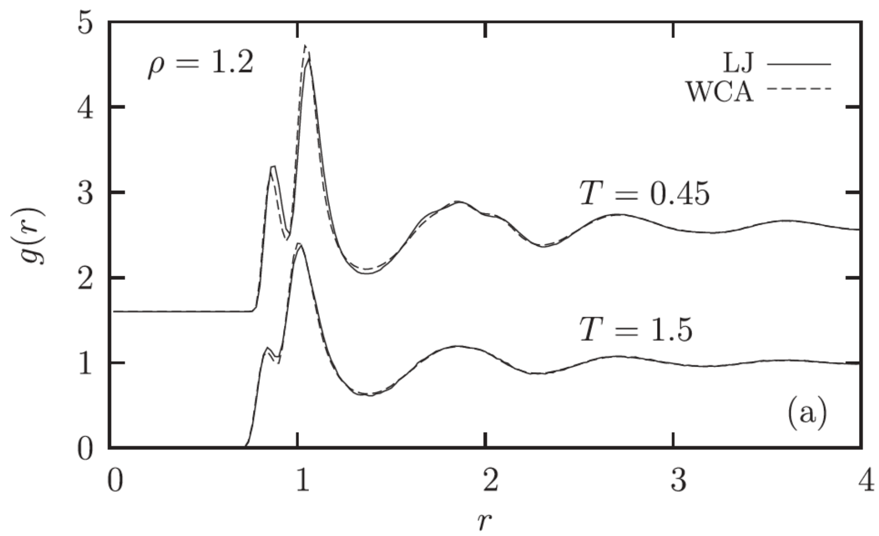
- Mode coupling theory → its success and failure
- From Structure to dynamics via entropy
- Molecular mean field theory

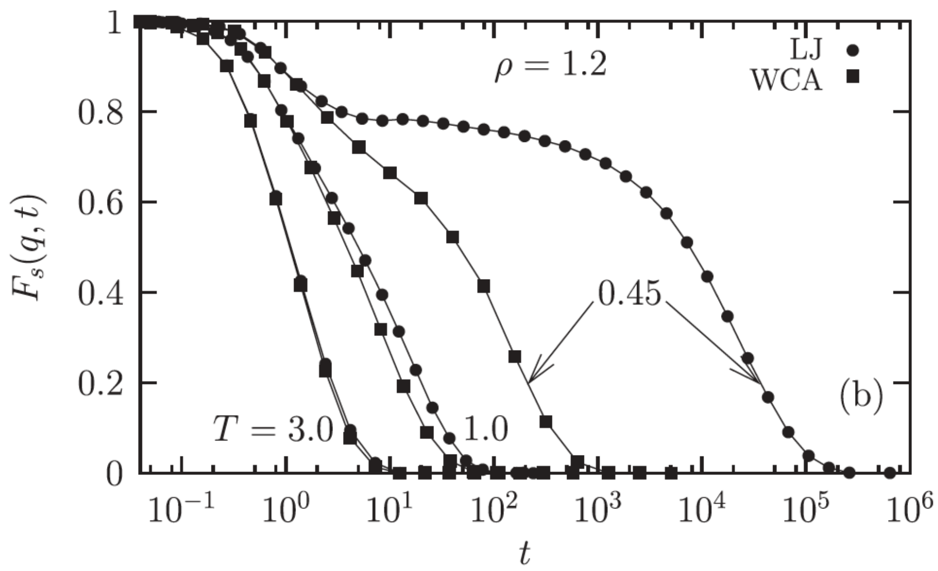
Similar Structure but difference in dynamics





Weeks, Chandler , Anderson, J. Chem. Phys. 54 5237 (1971)

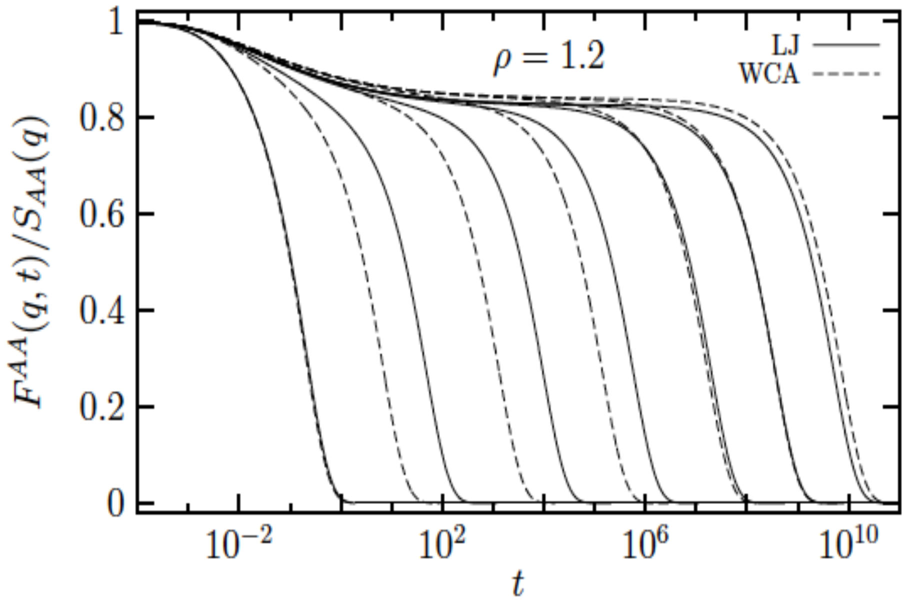


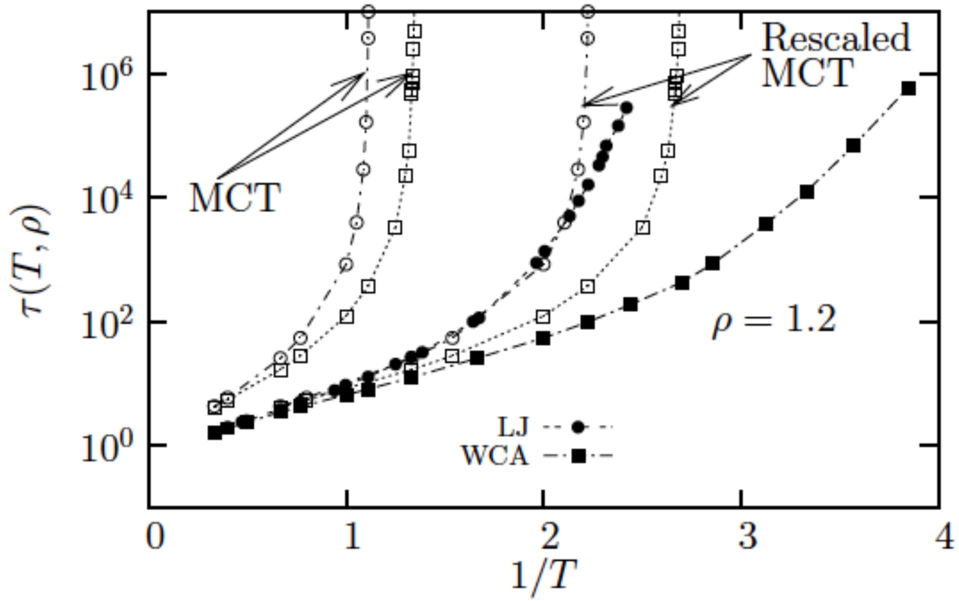


Can structure determine the difference in dynamics ??

Berthier & Tarjus, PRL **103**, 170601 (2009); PRE **82**, 031502 (2010); EPJE 34, 96 (2011) ; JCP 134, 214503 (2011)

Mode coupling theory (MCT) prediction





Microscopic MCT fails to predict simulated results

•Over estimated the temperature regime for slow dynamics

•Failed to predict the difference between the LJ and WCA system

Berthier & Tarjus, PRE **82**, 031502 (2010)

How a small difference in structure can account for a large difference in dynamics??

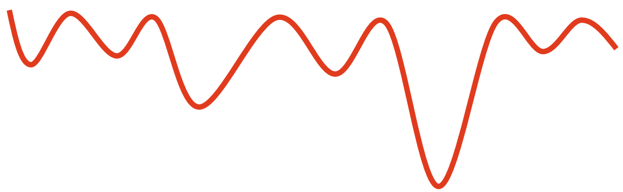
- The slow down of relaxation time purely kinetic in nature ??

- Difference in static pair correlation is small but can many body (higher order) static correlations explain the difference in dynamics ??

Thermodynamics or Kinetics ??

Need a thermodynamic marker

Configurational entropy

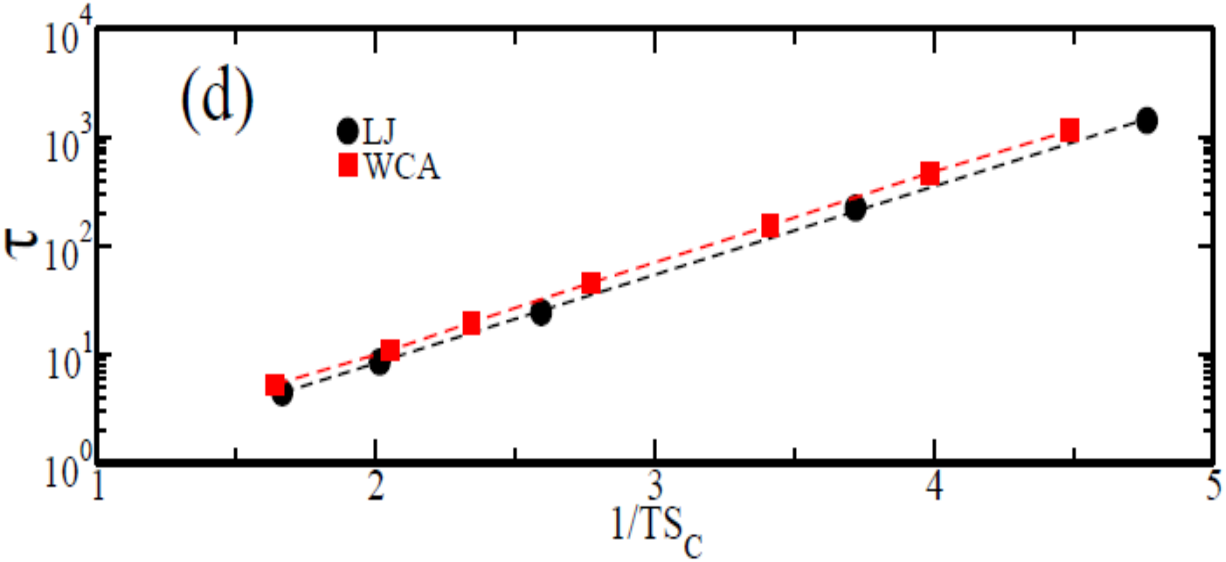


$$S_C = S_{total} - S_{vib} = S_{ideal} + S_{ex} - S_{vib}$$

Thermodynamics → Dynamics
Adam –Gibbs expression relates the dynamics to the configurational entropy → to the energy landscape

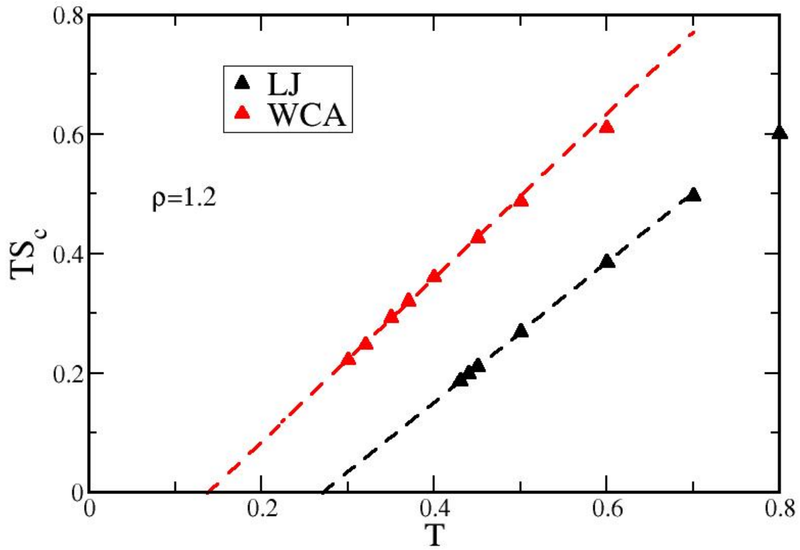
$$\tau(T) = \tau_0(T)\exp\left(\frac{A}{TS_c}\right)$$

Validity of Adam–Gibbs relation



$$\tau(T) = \tau_0(T)\exp\left(\frac{A}{TS_c}\right)$$

$$S_C = S_{ideal} + S_{ex} - S_{vib}$$



Difference in Thermodynamic→ Difference in Dynamics

A. Banerjee, S. Sengupta, S. Sastry, and S. M. Bhattacharyya, *Phys. Rev. Lett.* **113**, 225701 (2014).

Pair ??

Higher order ???

Entropy = Pair + Higher order

Configurational entropy

$$S_C = S_{total} - S_{vib} = S_{ideal} + S_{ex} - S_{vib}$$

Excess entropy per particle → Kirkwoods factorization

Nettleton & Green, JCP. **29**,1365(1958)

$$S_{ex} = S_{total} - S_{id} = S_2 + S_3 + ... = S_2 + \Delta S$$

ΔS → residual multi particle entropy (RMPE)

Pair excess entropy

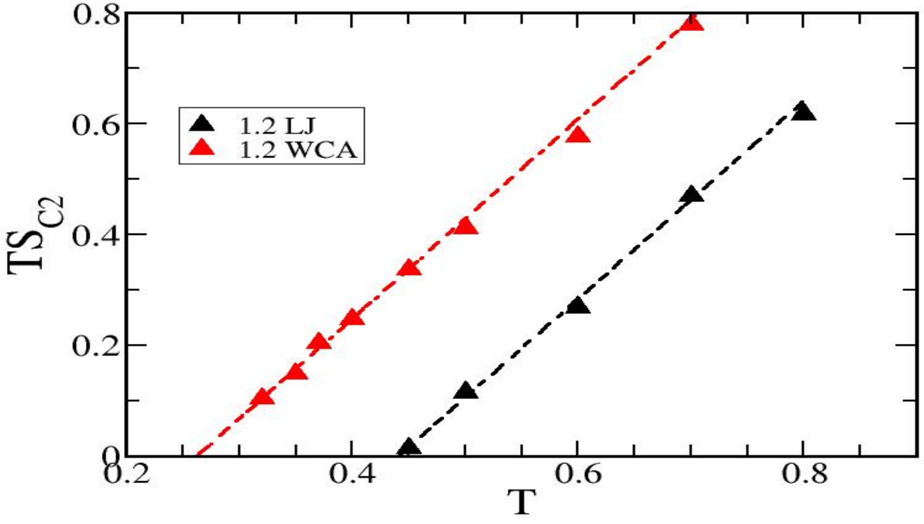
$$S_2 / k_B = -\frac{\rho}{2}\sum_{\alpha\beta} x_\alpha x_\beta \int d^3r \left[g_{\alpha\beta}(r) \ln\left[g_{\alpha\beta}(r) \right] - g_{\alpha\beta}(r) + 1 \right]$$

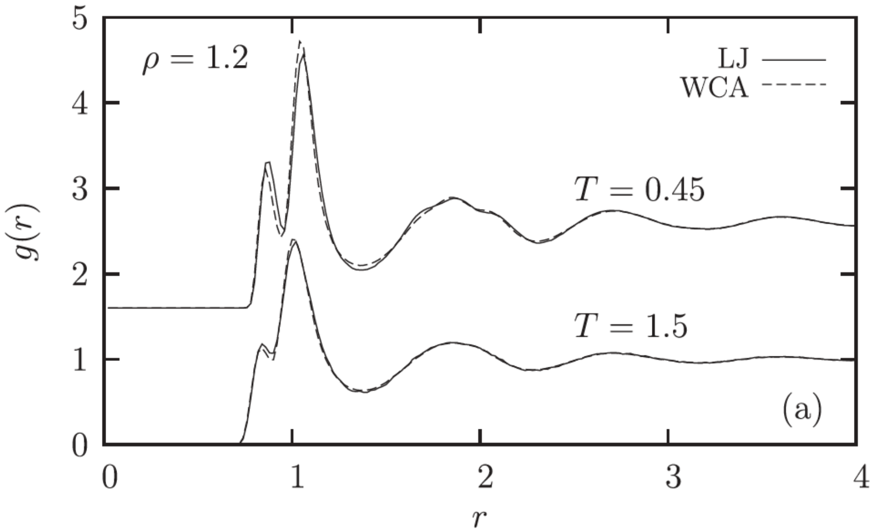
Pair configurational entropy

$$S_{C2} = S_{ideal} + S_2 - S_{vib}$$

A. Banerjee, S. Sengupta, S. Sastry, and S. M. Bhattacharyya, *Phys. Rev. Lett.* **113**, 225701 (2014).

Difference in thermodynamics even at the pair level

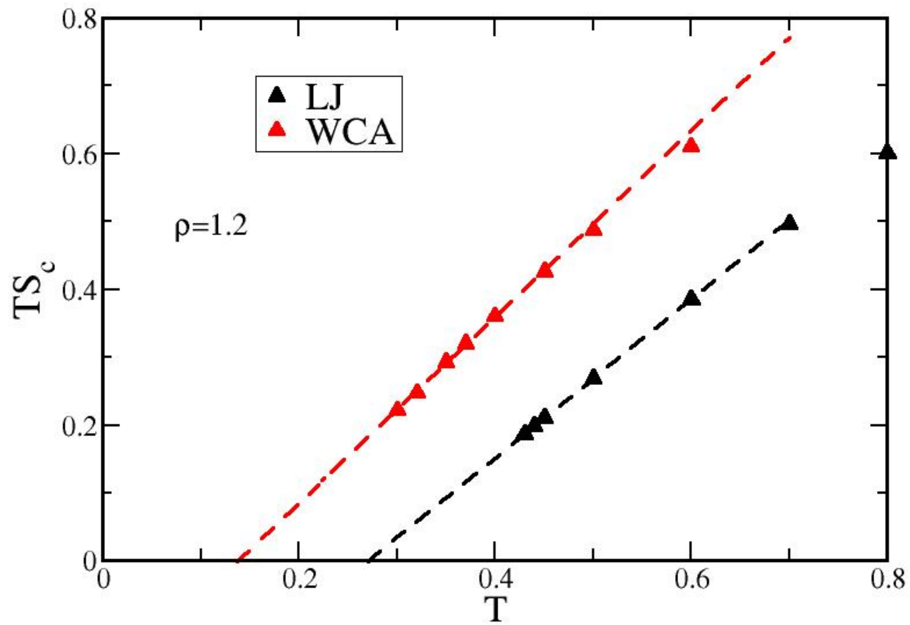




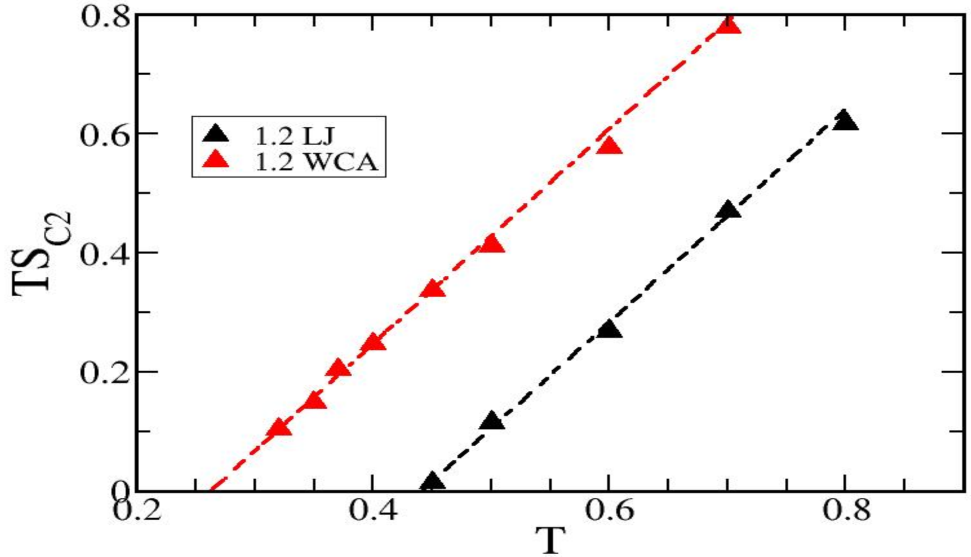
Small difference in structure leads to large difference in → pair configurational entropy → Dynamics

Kauzmann like temperature from S_{c2}

Extrapolated TS_c → Vanishes at T_K



Extrapolated TS_{c2} → Vanishes at T_{K2}



Critical temp from S_{c2}

	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

$$T_{K2} \sim T_c$$

????

Puzzle

Configurational entropy → Activated dynamics

MCT → mean field theory no activation

$$S_{C2} = S_{ideal} + S_2 - S_{vib}$$

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

Is the information of MCT transition temperature embedded in pair correlation function ?

Broad outline

- Mode coupling theory → its success and failure
- From Structure to dynamics via entropy
- Molecular mean field theory

The Theory: from Fokker Planck equation

Fokker-Planck equation for N-body distribution function

$$\frac{\partial P_N}{\partial t} = \sum_{i=1}^{N} \frac{\partial}{\partial \mathbf{r_i}} . \left[D_0 \frac{\partial P_N}{\partial \mathbf{r_i}} + \frac{P_N}{m\xi} \frac{\partial}{\partial \mathbf{r_i}} U(\mathbf{r_1}, ..., \mathbf{r_N}) \right]$$

$$P_N(\mathbf{r_1}, ..., \mathbf{r_N}) = \frac{1}{Z(\beta)} e^{-\beta u(\mathbf{r_1}, ..., \mathbf{r_N})}$$

N-body distribution function

$$Z(\beta) = \int e^{-\beta u(\mathbf{r_1}, ..., \mathbf{r_N})} d\mathbf{r_1} ... d\mathbf{r_N}$$

Partition function

Fokker-Planck equation for reduced distribution function

$$\frac{\partial P_j}{\partial t} = \sum_{i=1}^{j} \frac{\partial}{\partial \mathbf{r_i}} . [D_0 \frac{\partial P_j}{\partial \mathbf{r_i}} + \frac{P_j}{\xi} \sum_{k=1}^{j} \frac{\partial}{\partial \mathbf{r_i}} u_{i,k}$$

$$+ \frac{N-j}{\xi} \int P_{j+1} \frac{\partial}{\partial \mathbf{r_i}} u_{i,j+1} d\mathbf{r_{j+1}}]$$

Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy (BBGKY)

First equation of BBGKY hierarchy

$$\frac{\partial P_1}{\partial t} = \frac{\partial}{\partial r_1} \cdot \left[\frac{k_B T}{\xi} \frac{\partial P_1}{\partial r_1} + \frac{(N-1)}{\xi} \int P_2 \frac{\partial u_{12}}{\partial r_1} dr_2 \right]$$

Probability

$$\frac{\partial \rho(r_1)}{\partial t} = \frac{\partial}{\partial r_1} \cdot \left[\frac{k_B T}{\xi} \frac{\partial \rho(r_1)}{\partial r_1} + \frac{1}{\xi} \int \rho^{(2)}(r_1, r_2) \frac{\partial u_{12}}{\partial r_1} dr_2 \right]$$

Density

Mean Field Approximation

$$\rho(r) \frac{\partial}{\partial r} \Phi(r) = \int \rho^{(2)}(r, r') \frac{\partial u\left(\left|r - r'\right|\right)}{\partial r} dr'$$

$\boldsymbol{\Phi}(r)$ → Effective one body potential

Smoluchowski equation and Mean first passage time

$$\frac{\partial \rho(r_1)}{\partial t} = \frac{\partial}{\partial r_1} \cdot \left[\frac{k_B T}{\xi} \frac{\partial \rho(r_1)}{\partial r_1} + \frac{1}{\xi} \int \rho^{(2)}(r_1, r_2) \frac{\partial u_{12}}{\partial r_1} dr_2 \right]$$

Mean field approximation

$$\frac{\partial \rho(r)}{\partial t} = \frac{\partial}{\partial r} \cdot \left[\frac{k_B T}{\xi} \frac{\partial \rho(r)}{\partial r} + \frac{1}{\xi} \rho(r) \frac{\partial}{\partial r} \Phi(r) \right]$$ Smoluchowski equation

Dynamics of a set of non-interacting particles in an external potential

Mean first passage time

$$\tau = \frac{1}{D} \int dy e^{\beta \Phi(y)} \int dz e^{-\beta \Phi(z)}$$

Zwanzig , PNAS 85, 2029 (1988)

Describing the potential

$$\Phi(r) = \beta \frac{\delta F_{exc}(\rho(r))}{\delta \rho(r)}$$

Excess Free Energy → RY free energy functional

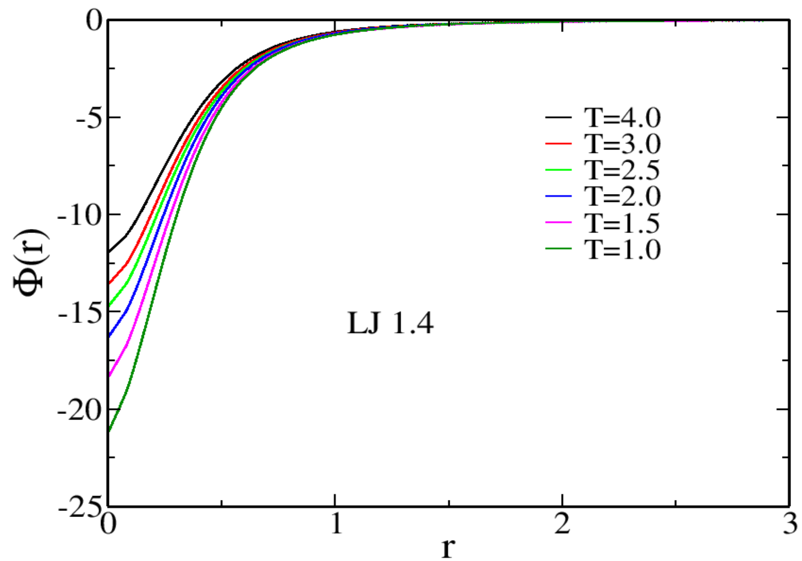
$$\beta F_{exc} \simeq -\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' \rho(r) C(|r-r'|)\rho(r')$$

Ramakrishnan et al PRB 19,2775

$$\rho(r,t) = (3/(2\pi r_i^2(t)))^{3/2} exp(-3r^2/2r_i^2(t))$$

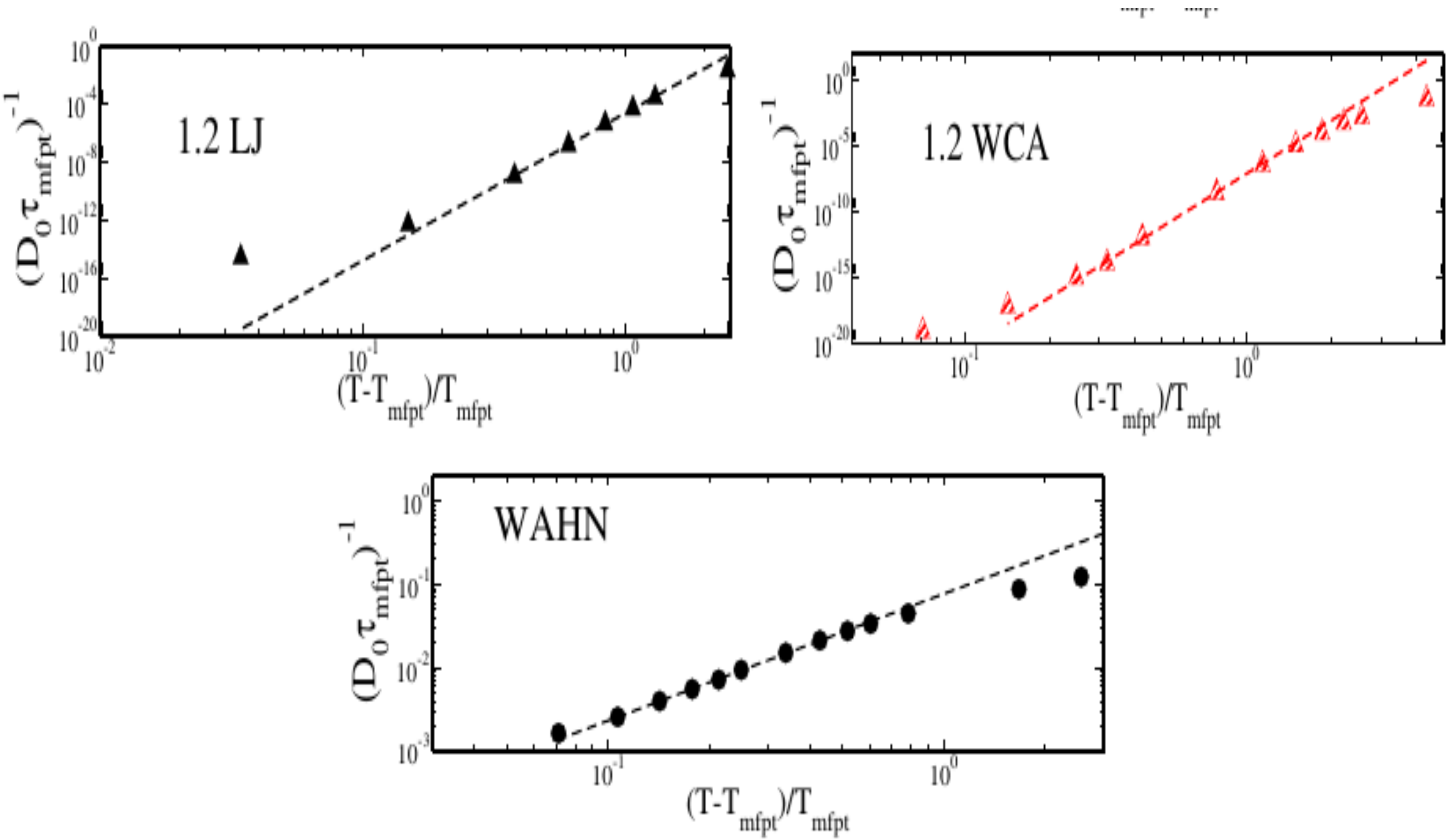
Kirkpatrick and Wolynes PRA **35**, 3072 (1987)
Schweizer et al. JCP **123**,244501 (2005)

$$\Phi(r) = \beta\frac{\delta F_{exc}}{\delta\rho} \simeq -\frac{1}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\rho C^2(q) S(q) e^{-q^2 r^2/3}$$



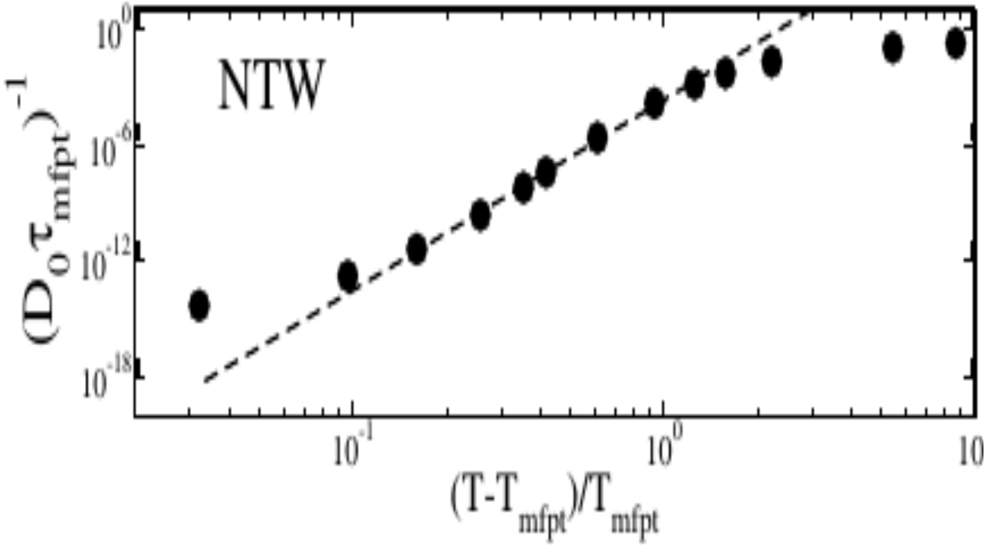
Mean field potential depends only on pair correlation function

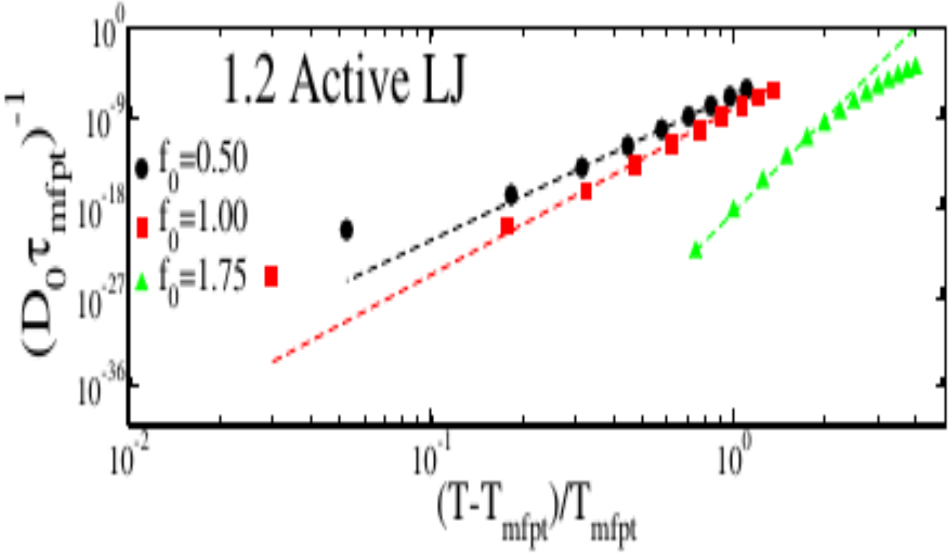
Power law behaviour and transition temperature



Power law behaviour and transition temperature

C. Dasgupta et al. (active system data)





T^*	KALJ			KAWCA			Active LJ			NTW	WAHN
	$\rho=1.2$	$\rho=1.4$	$\rho=1.6$	$\rho=1.2$	$\rho=1.4$	$\rho=1.6$	$f_0=0.50$	$f_0=1.00$	$f_0=1.75$		
T_{mfpt}	0.428 $\pm$0.022	0.94 $\pm$0.029	1.757 $\pm$0.042	0.283 $\pm$0.005	0.824 $\pm$0.04	1.691 $\pm$0.018	0.38 $\pm$0.004	0.335 $\pm$0.006	0.196 $\pm$0.013	0.308 $\pm$0.012	0.566 $\pm$0.013
T_c	0.435	0.93	1.76	0.28	0.81	1.69	0.39	0.34	0.19	0.31	0.56
T_c^{micro}	0.887	1.868	3.528	0.76	1.771	3.33	0.768	0.761	0.747	0.464	0.87

$$T_{mfpt} \sim T_C$$

Information of T_c is embedded in pair correlation function

M. Nandi, A. Banerjee, C. Dasgupta, S. M. Bhattacharyya (to be submitted)

Smoluchowski equation to MCT

$$\frac{\partial \rho(r)}{\partial t} = \frac{\partial}{\partial r} \cdot \left[\frac{k_B T}{\xi} \frac{\partial \rho(r)}{\partial r} + \frac{1}{\xi} \rho(r) \frac{\partial}{\partial r} \Phi(r) \right]$$

Smoluchowski equation

$$\Phi(r) = \beta \frac{\delta F_{exc}}{\delta \rho}$$

Excess Free Energy

$$\frac{\partial \rho(r)}{\partial t} = \frac{\partial}{\partial r} \cdot \left[\frac{k_B T}{\xi} \frac{\partial \rho(r)}{\partial r} + \frac{1}{\xi} \rho(r) \frac{\partial}{\partial r} \frac{\delta F_{exc}(\rho(r))}{\delta \rho(r)} \right]$$

Excess Free Energy → RY free energy functional

$$\beta F_{exc}(\rho) = \int d\mathbf{r} \int d\mathbf{r}' \rho(r) C^2(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$$

Smoluchowski Equation to MCT

$$\frac{\partial \delta\rho_k}{\partial t} = -\frac{k_B T k^2}{\xi}(1-\rho_0 C_k)\delta\rho_k(t) + \frac{k_B T}{2\xi}\int_q \mathbf{dq}[\mathbf{k}.\mathbf{q}C_q + \mathbf{k}.(\mathbf{k}-\mathbf{q})C_{k-q}]\delta\rho_q(t)\delta\rho_{k-q}(t)$$

Noise term

$$\gamma\frac{\partial \delta\rho_k(t)}{\partial t} + \frac{k_B T k^2}{S(k)}\delta\rho_k(t) + \int_0^t ds\mathcal{M}(k,t-s)\frac{\partial \delta\rho_k(t)}{\partial s} + \mathcal{R}_k(t) = 0$$

Langevin equation in non-Markovian limit

Fluctuation dissipation relation

$$\mathcal{M}(k,t) = \frac{<\mathcal{R}_k(t)\mathcal{R}_{-k}(0)>}{k_B T V} = \frac{1}{k_B T V}(\frac{k_B T}{2})^2\frac{1}{(2\pi)^6}\int \mathbf{dq}\mathbf{dq}'\hat{k}.[\mathbf{q}C_q + (\mathbf{k}-\mathbf{q})C_{k-q}]$$
$$\times\hat{k}.[\mathbf{q}C_q + (\mathbf{k}-\mathbf{q})C_{k-q}] < \delta\rho_q(t)\delta\rho_{k-q}(t)\delta\rho'_q(0)\delta\rho_{-k-q'}(0) >$$

Kawasaki, J. Stat. Phys., 110, 1249 (2002)

Smoluchowski Equation to MCT

Density-density correlation

$$\gamma \dot{F}(k,t) + \Omega_k^2 F(k,t) + \Omega_k^2 \int M(k,t-t')\dot{F}(k,t')\,dt' = 0$$

$$M(k,t) = \frac{\rho S(k)}{2k^2} \int \frac{d\vec{q}}{(2\pi)^3} V_k^2(\vec{q}, \vec{k}-\vec{q}) S(k-q) S(q) F(|\vec{k}-\vec{q}|,t) F(q,t)$$

Four point correlation → 2 two-point correlation

$$\left\langle \delta\rho_q(t)\delta\rho_{k-q}(t)\delta\rho_q(0)\delta\rho_{-k-q}(t) \right\rangle$$

Conclusions

- $T_c^{micro} > T_c$
- S_{c2} predicts T_c
- Dynamics of the mean field predits T_c
- Information of T_c embedded in pair correlation function
- Smoluchowski Equation to MCT Equation→ MCT failure is due to the approximations

Thank you