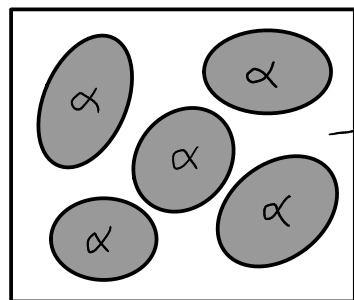


Modello di Adam e Gibbs 1965

CRR \equiv cooperatively rearranging regions



$\alpha = n$ - di stati per CRR
 $n = n$ - di particelle per CRR
 $N = n$ - particelle totali

Stati accessibili

$$\Omega = \alpha^{N/n}$$

Entropia configurazionale

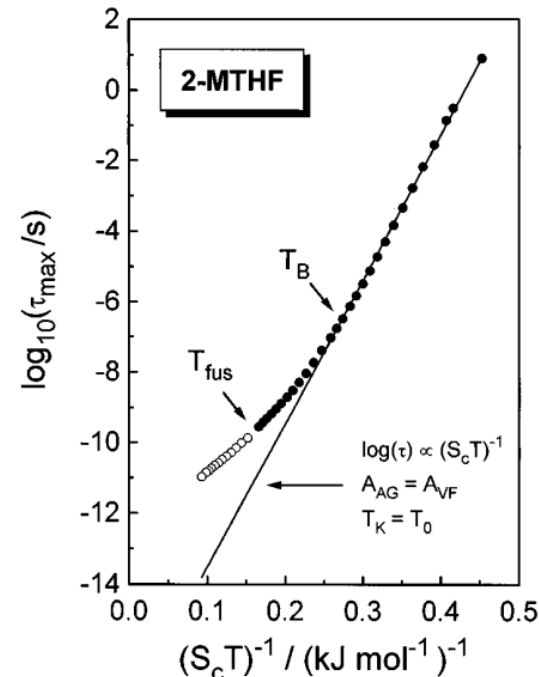
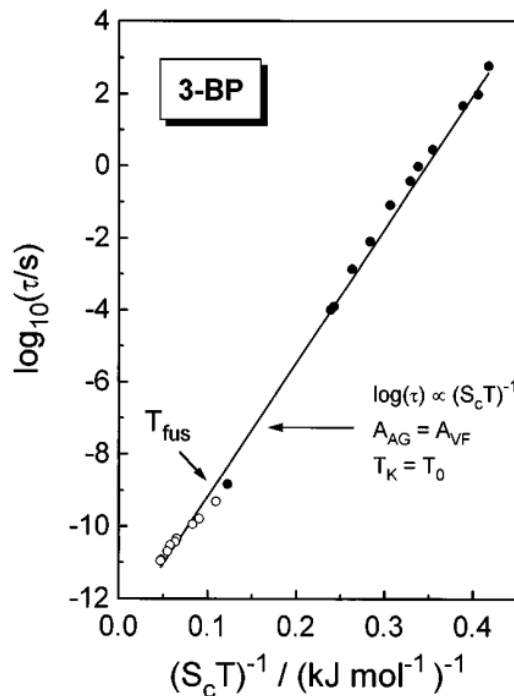
$$S_c = \frac{1}{N} k_B \ln \Omega = \frac{k_B}{n} \ln \alpha$$

$$n \sim \frac{1}{S_c}$$

Tempo rilassamento strutturale

$$\tau_\alpha = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right) \approx \tau_0 \exp\left(\frac{A}{T S_c}\right)$$

$\Delta E \sim n \sim \frac{1}{S_c}$ \nearrow relazione Adam-Gibbs



Richert & Angell JCP 1998

Vicino a T_K (ipotetica)

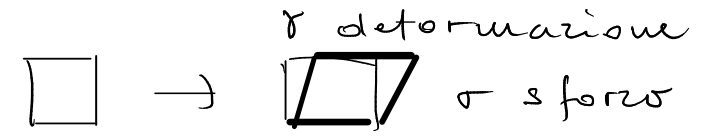
$$S_c \sim \frac{1}{T_K} (T - T_K) \quad T_K \gg 0 \quad T \approx T_K$$

$$\tau_\alpha = \tau_0 \exp\left(\frac{A T_K}{T(T - T_K)}\right) \approx \tau_0 \exp\left(\frac{A}{T - T_K}\right)$$

legge di Vogel-Fulcher-Tammann

Teoria mode-coupling

1) 2-steps relaxation + stretched exponential



Solido Hookiano $\sigma = G_0 \gamma$

liquido Newtoniano $\sigma = \eta \dot{\gamma}$

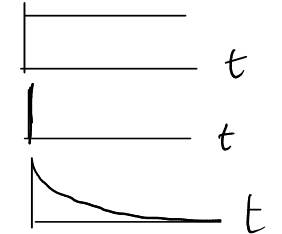
modello Maxwell $\sigma = \int_{-\infty}^t G(t-s) \dot{\gamma}(s) ds$

$G(t) = G_0$

$G(t) = \eta \delta(t)$

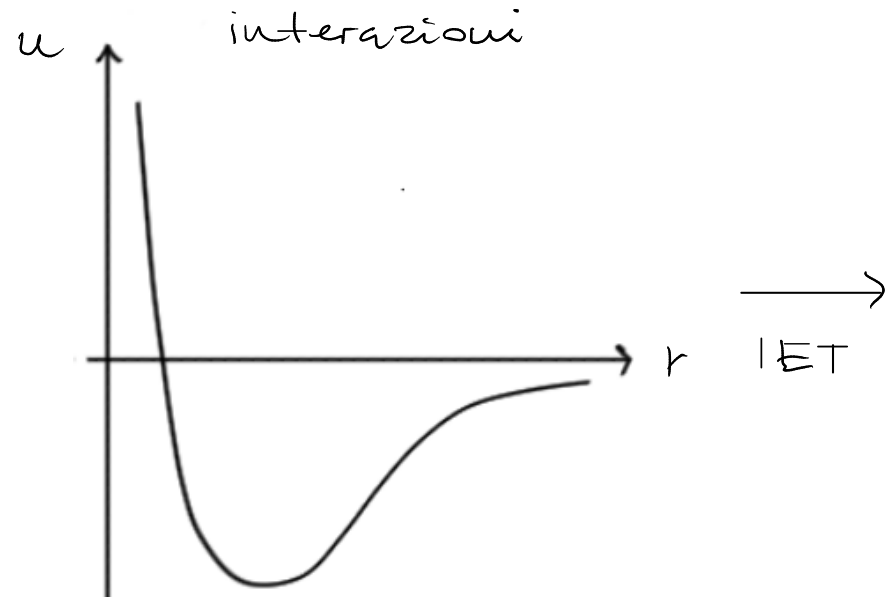
$G(t) = G_0 \exp(-t/\tau)$ (BH)

$t \ll \tau$ solido $t \gg \tau$ liquido

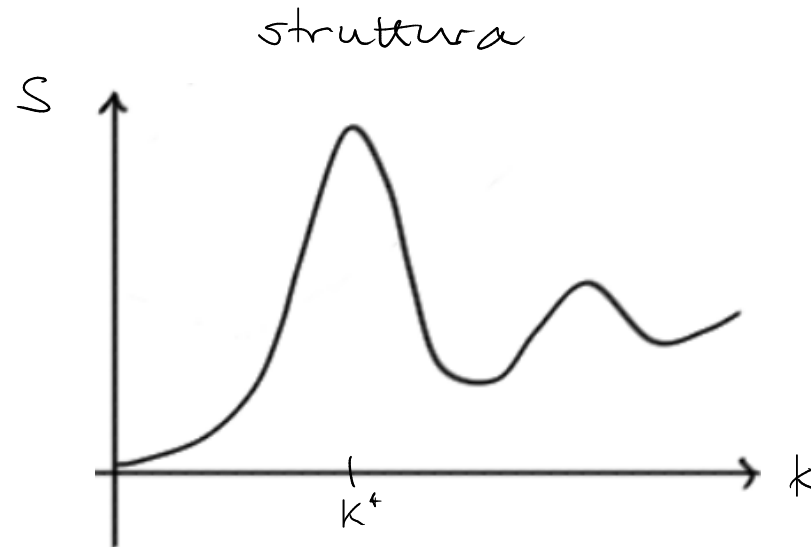


2) $\tau_\alpha(T)$ \exists transizione a T finita?

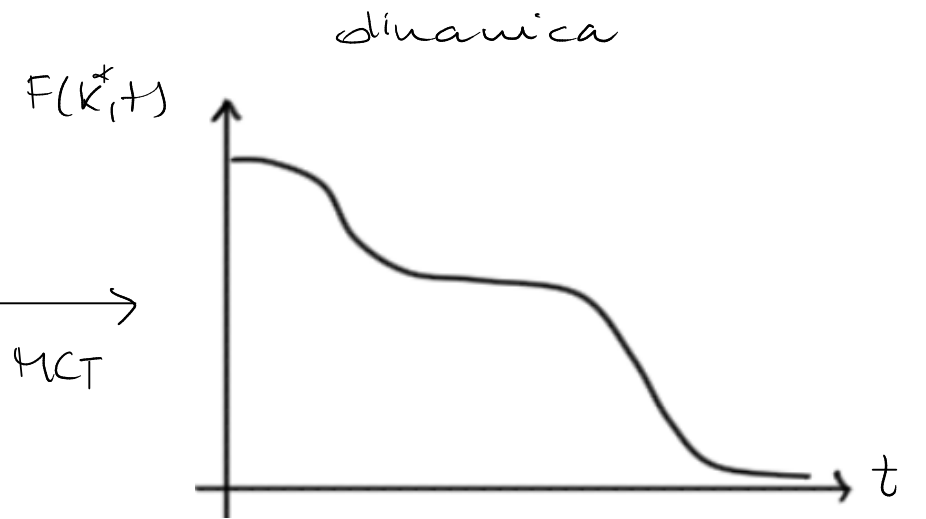
MCT 1984 Götze + collaboratori microscopica + principi primi



$\xrightarrow{\text{IET}}$



$\xrightarrow{\text{MCT}}$



Eq. moto esatta per osservabili dinamiche $A(t)$

osservabili lente $g_{\vec{k}}(t), J_{\vec{k}}(t)$ → formalismo operatore proiezione Mori-Zwanzig
osservabili veloci $(A, B) \equiv \langle B A^* \rangle$

Eq. Langevin generalizzata

$$\frac{dA}{dt} = i\Omega A(t) - \int_0^t M(t-s) A(s) ds + \Theta(t) \leftarrow \text{forza stocastica } (\Theta(t), A) = 0$$

\uparrow $i\Omega = \frac{(A, \dot{A})}{(A, A)}$ \uparrow funzione di memoria → autocorrelazione di $\Theta(t)$

$$C(t) = \frac{\langle A(t) A^*(0) \rangle}{\langle A A^* \rangle}$$

$$\frac{dC}{dt} = i\Omega C(t) - \int_0^t M(t-s) C(s) ds \quad \text{esatta ma insolubile}$$

Funzione intermedia scattering : $F(k, t) = \frac{\langle g_{\vec{k}}(t) g_{\vec{k}}(0) \rangle}{\langle g_{\vec{k}} g_{-\vec{k}} \rangle}$

$$\frac{d^2 F}{dt^2} + \frac{K_B T K^2}{m S(K)} F(k, t) + \int_0^t ds M(k, t-s) \frac{dF}{ds}(k, s) = 0$$

\downarrow
 Ω^2

Mode-coupling : $M(k,t) \sim \int_{k_1}(t) \int_{k_2}(t)$

$$M(k,t) = \frac{\beta k_B T}{16 \pi^3 m} \int d\bar{k}' |V_{\bar{k}, \bar{k}-\bar{k}'}|^2 F(k,t) F(|\bar{k}-\bar{k}'|, t)$$

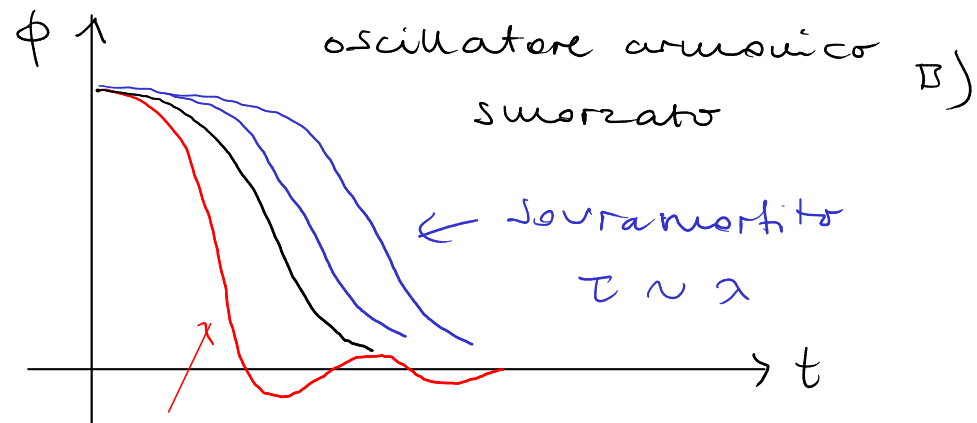
vertice
 $\rightarrow S(k)$

Versione schematica

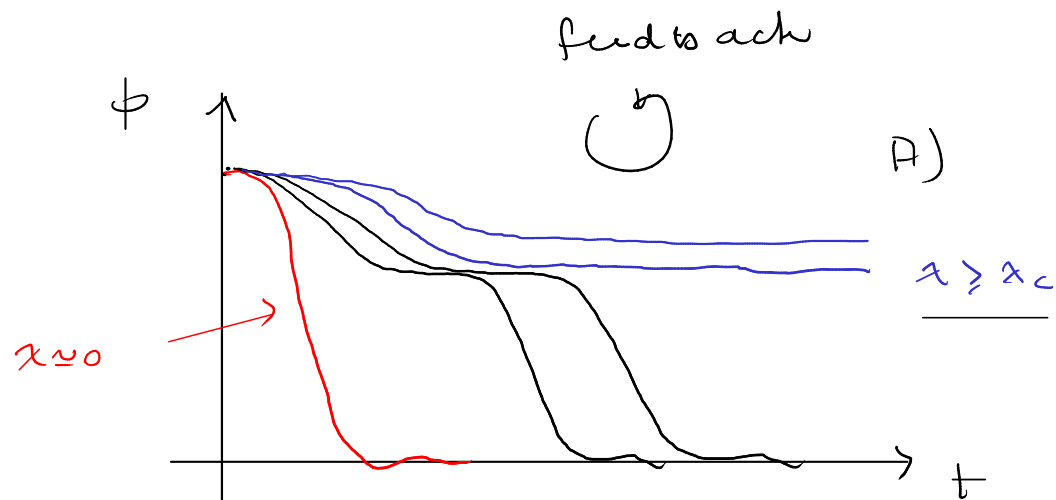
$$\phi(t) = F(k^k, t)$$

A) $\ddot{\phi} + \Omega^2 \phi(t) + \lambda \int_0^t ds \phi^2(t-s) \dot{\phi}(s) = 0$

B) $\ddot{\phi} + \Omega^2 \phi(t) + \lambda \dot{\phi}(s) = 0$



sottoammortito



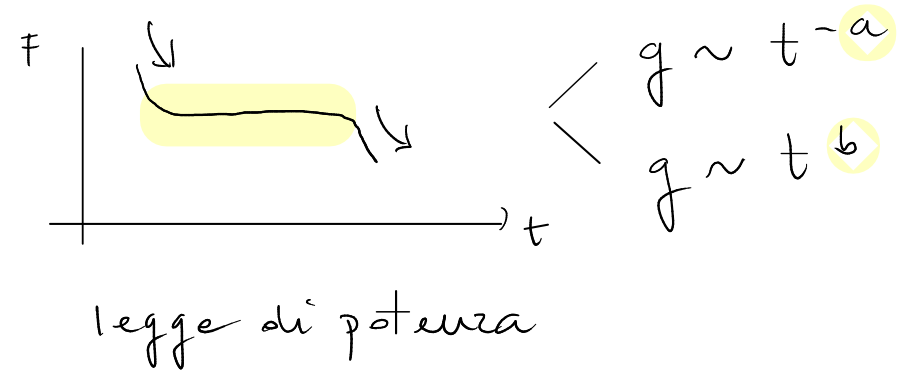
$\phi(t \rightarrow \infty) = f$
 fattore di non ergodicit 

Predizioni generali della MCT

1) **2-step** $T_c \rightarrow \infty$

- β -relaxation \rightarrow vicino al plateau

$$F(k,t) \approx \underbrace{f(k)}_{\text{plateau}} + \sqrt{|T-T_c|} \underbrace{h(k)}_{\text{plateau}} g(t/\tau_\beta)$$



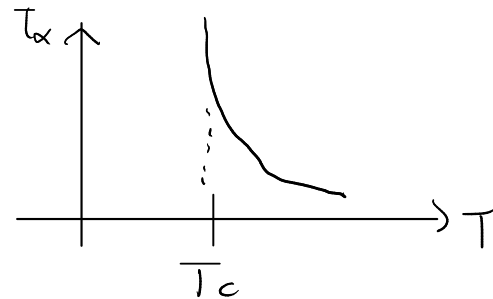
- α -relaxation

$$F(k,t) \approx \exp[-(t/\tau_\alpha)^{\beta'}]$$

MCT $k \rightarrow \infty$ k finito \checkmark $\beta' \sim 0.6 - 0.7$

2) $\tau_\alpha(T)$?

$$\begin{cases} \tau_\alpha \sim \frac{1}{|T-T_c|^\gamma} & \gamma \sim 2 \\ \tau_\beta \sim \frac{1}{|T-T_c|^{2a}} \end{cases}$$



3) $F_s(k,t)$, η , ...

Verifica predizioni MCT

1) "Principi primi" $S(K) \rightarrow F(k,t)$

T_c è troppo alta $\sim T_{ouset}$ miscela binaria Kob-Anderson $T_{ouset} \sim 0.8-1.0$

MCT \sim teoria campo medio

$$T_c^{(PP)} = 0.92$$

$$T_g^{(chim)} = 0.4$$

2) "Fit" T_c e γ, a, b parametri liberi

$$K-A \quad T_c^{(fit)} \approx 0.435 \quad (Kob)$$

$$T_{ouset} > T_c^{(fit)} > T_K$$

