

Applying the replica approach to structural glasses: the silica case

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- A theoretical approach to structural glass thermodynamics
- The molecular liquid
- The harmonic approximation
- Results for a LJ binary mixture
- The silica case

Critical Temperatures

- The experimental glass transition temperature T_g is defined as the temperature where the viscosity is $\eta \sim 10^{13}$ Poise.
- The Mode Coupling dynamical critical temperature T_D is evaluated by fitting data on the viscosity with a power law of the form $\eta \propto (T - T_D)^\delta$.
- The Kauzmann temperature T_K , where the entropy of the liquid would become lower than the one of the solid.
- Fragile supercooled liquids: the viscosity is well described by the Vogel-Fulcher-Tamman law $\eta \propto \exp(A/(T - T_0))$.
- Strong supercooled liquids: the viscosity seems to follow the classical Arrhenius law $\eta \propto \exp(A/T)$.

$$T_D > T_g > T_K \simeq T_0$$

Theoretical approach

(Monasson, PRL **75**, 2847 (1995); Mézard and Parisi, PRL **82**, 747 (1998); J. Chem. Phys. **111**, 1076 (1999); Mézard, *Physica A* **265**, 352 (1999))

- Below T_D , the dynamics is dramatically slow because of the **exponentially** large number $\mathcal{N}(f) = e^{N\Sigma(f)}$ of *free energy minima* (*valleys*), where the system spend most of the time.
- The *valleys* must be thought as objects somewhat more complicated than the *inherent structures*, since a *valley* should be stable also against a **finite** rearrangement of a **non extensive** number of particles.
- One can write the **partition function** as a sum of contributions from different *valleys*:

$$Z = e^{-\beta N\phi(T)} = \int df e^{-\beta N f} \mathcal{N}(f).$$

- The *valleys* reached at equilibrium are not the lowest available but instead the ones which free energy f^* minimizes the following generalized free energy:

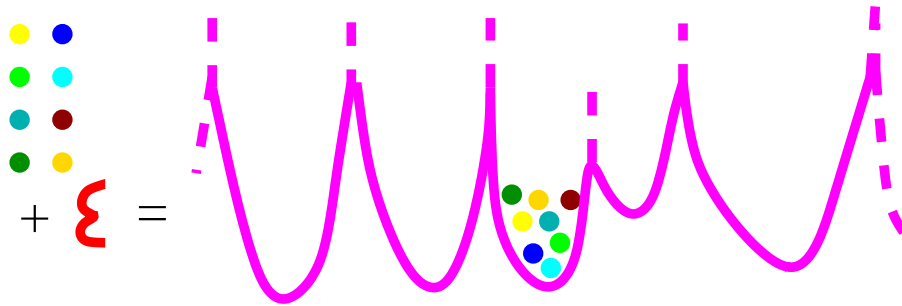
$$\phi(T) \sim \min_f [f - T\Sigma(f, T)].$$

- The scenario is very similar to the old Adam-Gibbs-Di Marzio one. One finds a **second order liquid-glass thermodynamic transition** corresponding to an “**entropy crisis**” at the Kauzmann temperature T_K where the **configurational** part of the entropy Σ vanishes.
- The free energy barriers between *valleys* have a finite height and can be overcome by means of **nucleation processes**, nevertheless one expects that the **approximation** becomes increasingly better for $T \rightarrow T_K$.
- At T_K the symmetry is broken in a discontinuous way, the system undergoing a **one step replica symmetry breaking**.

The replicated free energy

- One considers m copies (replicas) of the system

$$\mathcal{H}_{tot} = \sum_{a=1}^m \mathcal{H}[C^a]$$



- One introduces an attractive coupling term which forces them to stay in the same valley

$$\mathcal{I} \propto \epsilon \sum_{a,b} (\text{distanza}_{ab})^2$$

- One computes the partition function

$$\mathcal{Z} = \int \left(\prod_{a=1}^m \mathcal{D}[C^a] \right) \exp(-\beta \mathcal{H}_{tot} - \mathcal{I})$$

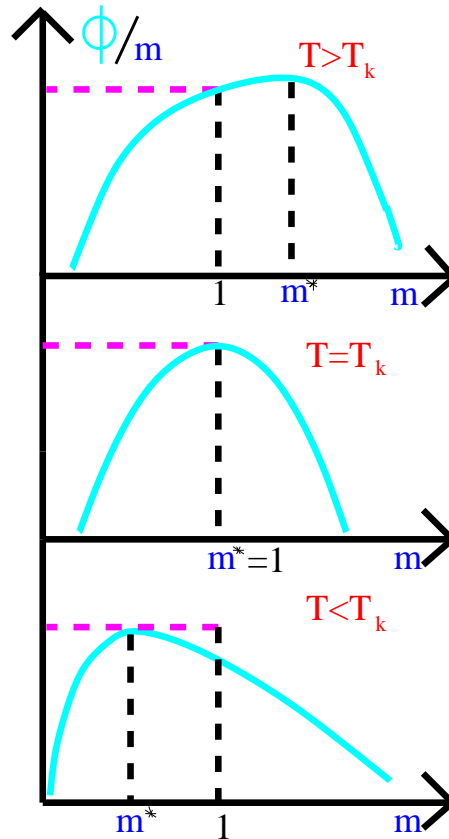
- In the $\epsilon \rightarrow 0$ limit,

$$\frac{1}{N} \log \mathcal{Z} = \phi(m, T) = \min_f [mf(T) - T\Sigma(f, T)]$$

- Therefore

$$\frac{\partial \phi(m, T)}{\partial m} = f \quad \frac{m^2}{T} \frac{\partial (\phi(m, T)/m)}{\partial m} = \Sigma$$

- $\phi(m, T)/m$ is a convex function of m which has a maximum in $m = m^*$.
- For $T > T_K$ one has $m^* > 1$ and the physical solution is the one with $m = 1$.
- At $T = T_K$ one has $m^* = 1$ and $\Sigma = 0$.



- In the $T < T_K$ region
 - m^* is lesser than 1.
 - Solutions with $m > m^*$ and in particular with $m = 1$ would give $\Sigma < 0$ (Kauzmann paradox).
 - One get the physical solution by taking

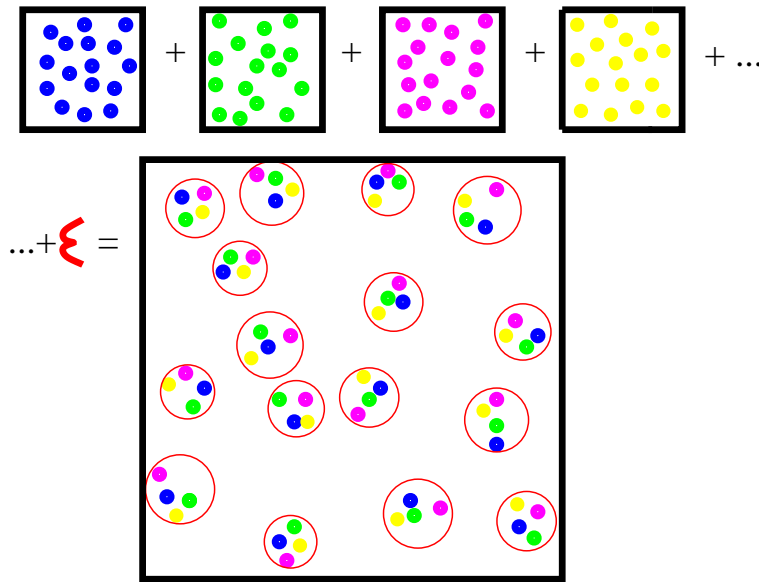
$$\phi(m, T)/m = \phi(m^*, T)/m^* = f_{min}(T),$$

i.e. the lowest possible free energy and $\Sigma = 0$ in the whole interval $[m^*, 1]$,

$$\phi(m, T)/m = \phi(m^*, T)/m^* = f_{min}(T),$$

Molecular liquid

$$\mathcal{H}[\{r_i\}] = \sum_{i < j=1}^N V(r_{ij}) \quad \mathcal{H}_{tot} = \sum_{a=1}^m \mathcal{H}[\{r_i^a\}]$$



- At $T < T_D$, in presence of the **attractive term**, one find molecules of m atoms, each one belonging to a different replica.
- One can choose a permutation

$$\mathcal{I} = \frac{\epsilon}{4} \sum_{a,b=1}^m \sum_{i=1}^N (r_i^a - r_i^b)^2$$

- It is useful to take as coordinates the centers of mass of molecules and the (small) **distances** of single atoms from these

$$R_i = \frac{1}{m} \sum_{a=1}^m r_i^a \quad r_i^a = R_i + u_i^a.$$

Harmonic approximation

$$\mathcal{Z} = \frac{1}{N!} \int \mathcal{D}[R] \mathcal{D}[u] \prod_{i=1}^N \left[m^d \delta \left(\sum_{a=1}^m u_i^a \right) \right] \cdot \exp \left[-\beta \sum_{a=1}^m \sum_{i < j=1}^N V(R_i - R_j + u_i^a - u_j^a) - \frac{\epsilon}{4} \sum_{a,b=1}^m \sum_{i=1}^N (u_i^a - u_i^b)^2 \right]$$

By expanding V up to **second order** and by integrating on $\{u_i^a\}$, one has

$$\propto \int \mathcal{D}[R] \exp \left[-\beta m \sum_{i < j} V(R_i - R_j) - \frac{m-1}{2} \text{Tr} \log (\beta \mathbf{M}) \right]$$

where

$$\mathbf{M}_{(i\mu)(j\nu)} = \delta_{ij} \left(\sum_k V_{\mu\nu}(R_i - R_k) + \epsilon m \right) - V_{\mu\nu}(R_i - R_j),$$

with $V_{\mu\nu} = \partial^2 V / \partial r_{i\mu} \partial r_{j\nu}$.

$$\int \mathcal{D}[R] \exp \left[-\beta m \sum_{i < j} V(R_i - R_j) \right] = \mathcal{Z}_{liq}(\beta m)$$

The molecular centers of mass interact at the temperature $T_{eff} = 1/(\beta m)$.

“**Quenched**” approximation:

$$\begin{aligned} \mathcal{Z} &\sim \mathcal{Z}_{liq}(\beta m) \left\langle \exp \left(-\frac{m-1}{2} \text{Tr} \log \beta \mathbf{M} \right) \right\rangle_{\beta m} \sim \\ &\sim \mathcal{Z}_{liq}(\beta m) \exp \left(-\frac{m-1}{2} \langle \text{Tr} \log \beta \mathbf{M} \rangle_{\beta m} \right). \end{aligned}$$

Within this approximation one has

$$\begin{aligned}\Sigma(\beta) &= \beta \left(m^2 \frac{\partial \phi(m, \beta)}{\partial m} \right)_{m=1} = \\ &= \beta^2 \frac{\partial \log Z_{liq}(\beta)}{\partial \beta} - \left(\frac{d}{2} (1 + \log(2\pi)) - \frac{1}{2N} \langle Tr \log(\beta M) \rangle_{\beta m} \right) = \\ &= S_{liq}(\beta) - S_{sol}(\beta),\end{aligned}$$

The Kauzmann temperature where $\Sigma \rightarrow 0$ is the one where the liquid entropy becomes equal to the harmonic entropy of corresponding amorphous solid.

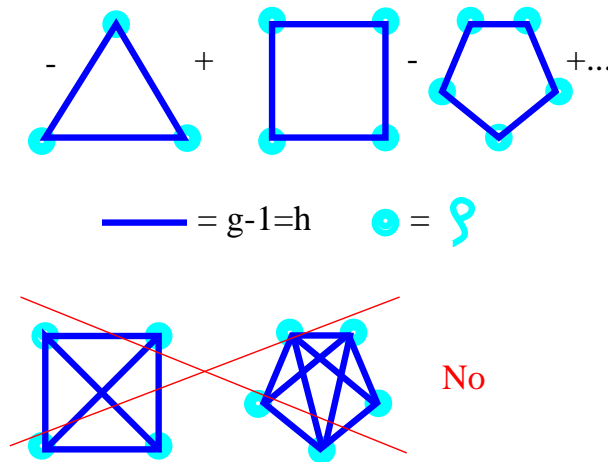
Extension to binary mixtures

(Coluzzi, Mézard, Parisi and Verrocchio, *J. Chem. Phys.* **111**, 9039 (1999))

- Molecules can be formed only by atoms of the same kind \Rightarrow two couplings and two independent order parameters.
- We take fluctuation of the diagonal term up to second order.
- We sum up the non diagonal contribution at all orders by using a chain approximation.

An approximation for the liquid

- The **HNC** approximation consists in summing up “chain” diagrams in the Mayer expansion, neglecting the “bridge” ones.



- It was often used successfully for studying potentials with a **Coulomb term**.
- There are some **thermodynamic inconsistencies**, which turn out in an overestimation of the **liquid-gas transition temperature T_{GL}** :

$$\rho\chi_1 = \beta + \rho\beta \int d^3r h(r) \neq \rho\chi_2 = \left(\frac{dP}{d\rho} \right)^{-1}$$

- The **ZH** approach allows to reduce this inconsistency by interpolating between **HNC** and **MSA**.

Lennard Jones binary mixture

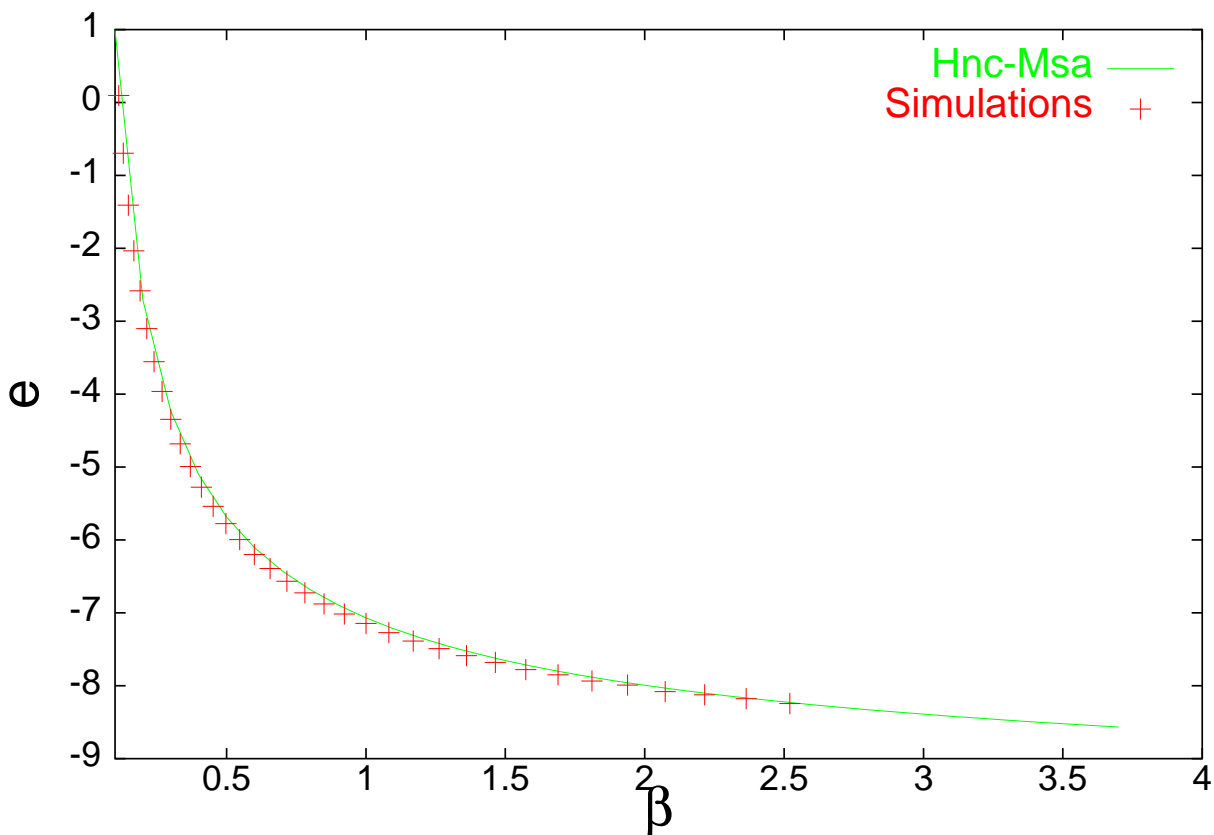
(Coluzzi, Parisi and Verrocchio, *J. Chem. Phys.* **112**, 2933 (2000); PRL **84**, 306 (2000); cond-mat/0007144)

$$V^{\alpha\beta}(r) = 4 \epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right]$$

$$\epsilon_{++} = 1, \quad \epsilon_{+-} = 1.5, \quad \epsilon_{--} = 0.5,$$

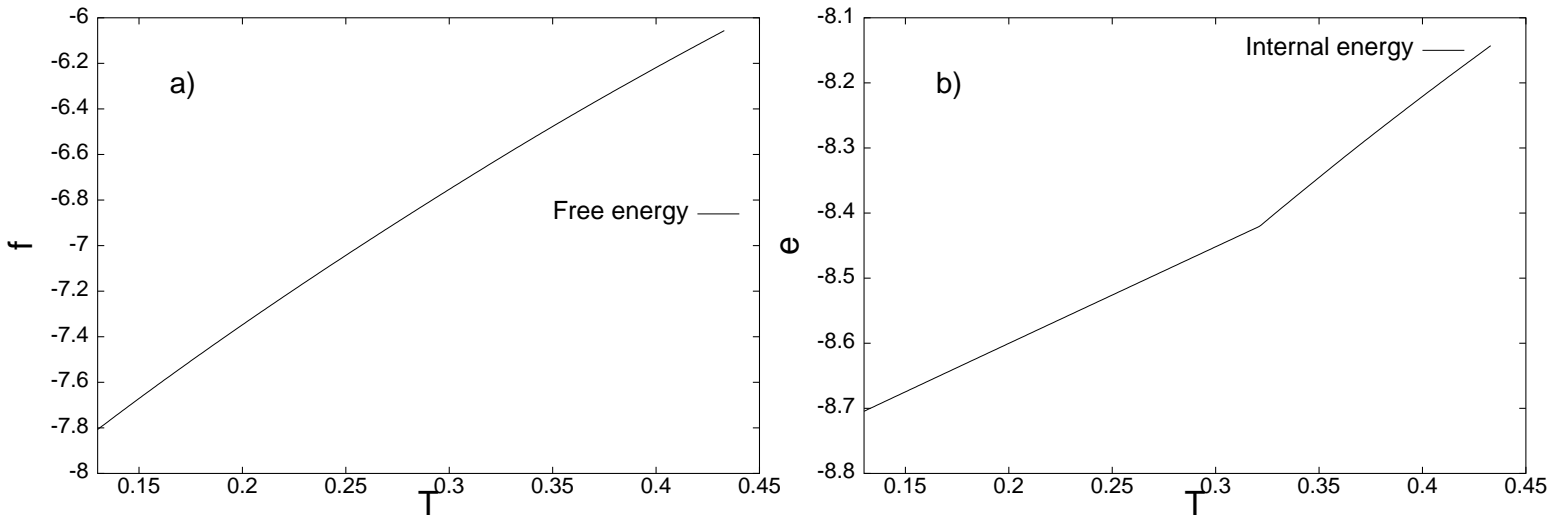
$$\sigma_{++} = 1, \quad \sigma_{+-} = 0.8, \quad \sigma_{--} = 0.88,$$

- $\rho = 1.2$.
- $c_+ = 4/5$.
- $T_{MCT} \simeq 0.435$.

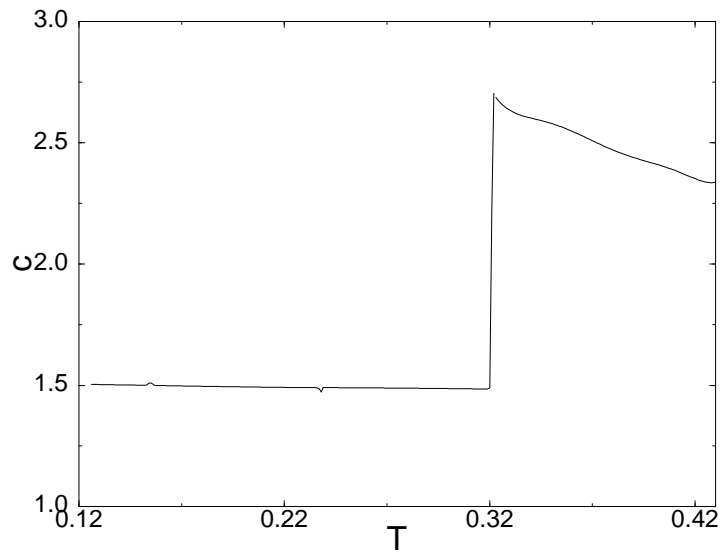


Results

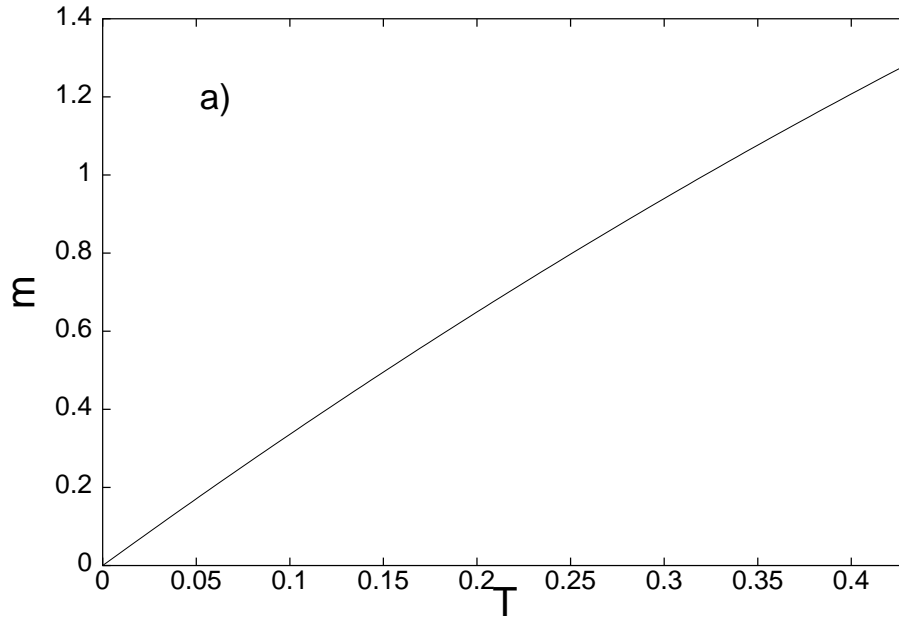
- II order liquid-glass transition at $T_K = 0.32$.



- Specific heat which follows the Dulong and Petit law in the glassy phase.

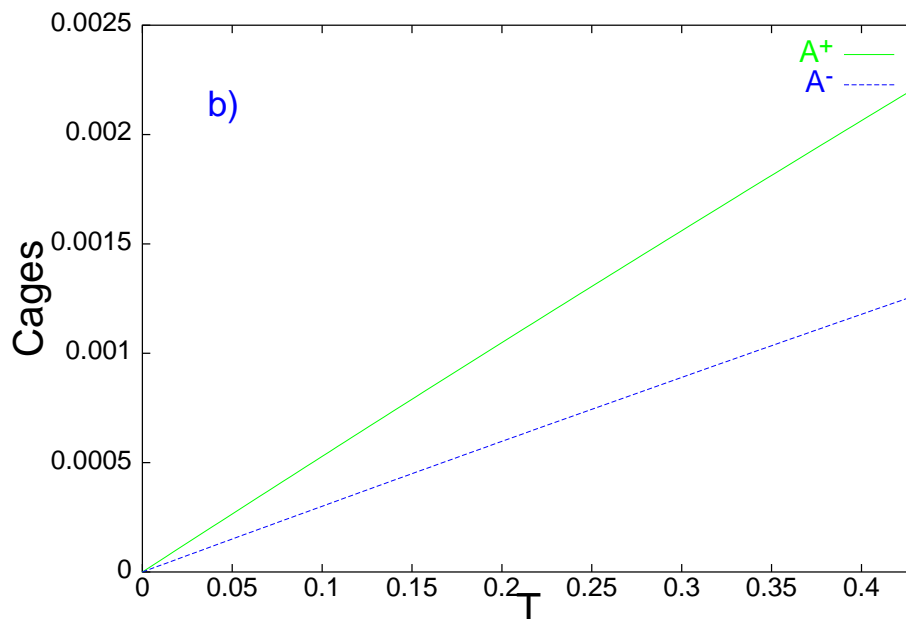


$$m \propto T \implies \beta m \sim \text{cost} \sim \frac{1}{T_K}$$



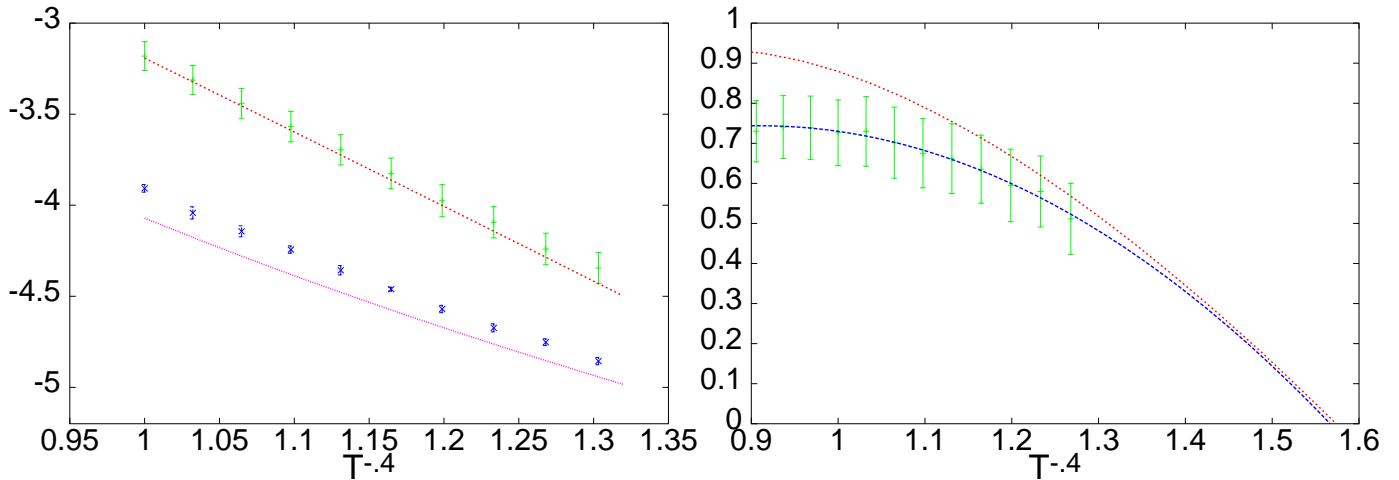
Order parameters

$$A_\alpha = \frac{1}{3}(\langle x_i^2 \rangle - \langle x_i \rangle^2) = \frac{2}{d(m-1)N_\alpha} \frac{\partial(\beta\phi)}{\partial\epsilon}(\epsilon=0)$$



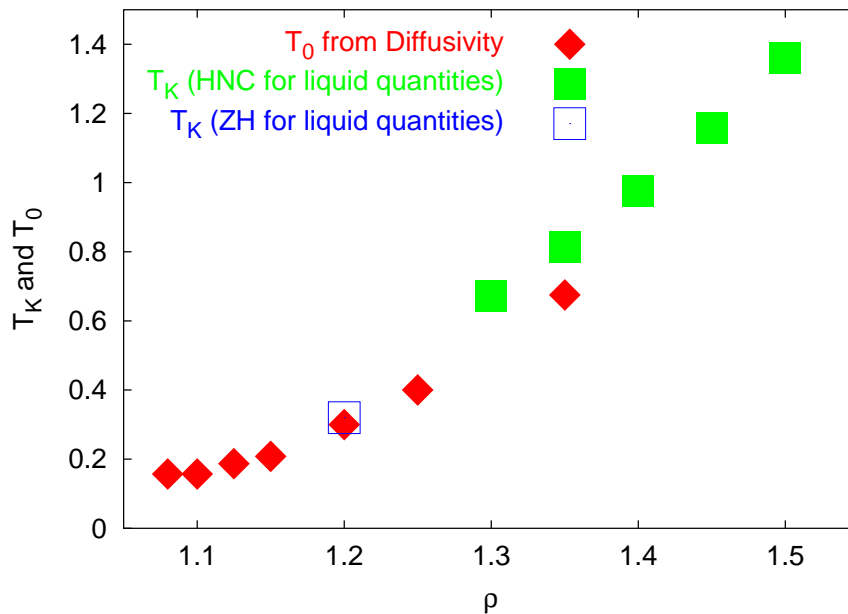
Comparison between Theory and Simulations

$$\Sigma = S_{liq} - S_{sol}$$



By extrapolating one finds $T_K = 0.32 \pm 0.04$ from simulations, in agreement with the evaluation $T_K = 0.297 \pm 0.02$ obtained by Sciortino, Kob and Tartaglia (PRL **83**, 3214 (1999)).

$$T_K(\rho)$$



T_K at different density values compared with the evaluations of T_0 obtained by Sastry (PRL **85**, 590 (2000)).

Silica

- $T_g \sim 1446K$ [?].
- They are supposed to belong to the class of **strong liquids**, though deviations from the **Arrhenius** plot above T_g have been observed.
- They are composed by molecules of SiO₂ which form **an open network of tetrahedra** at low temperatures.

BKS model

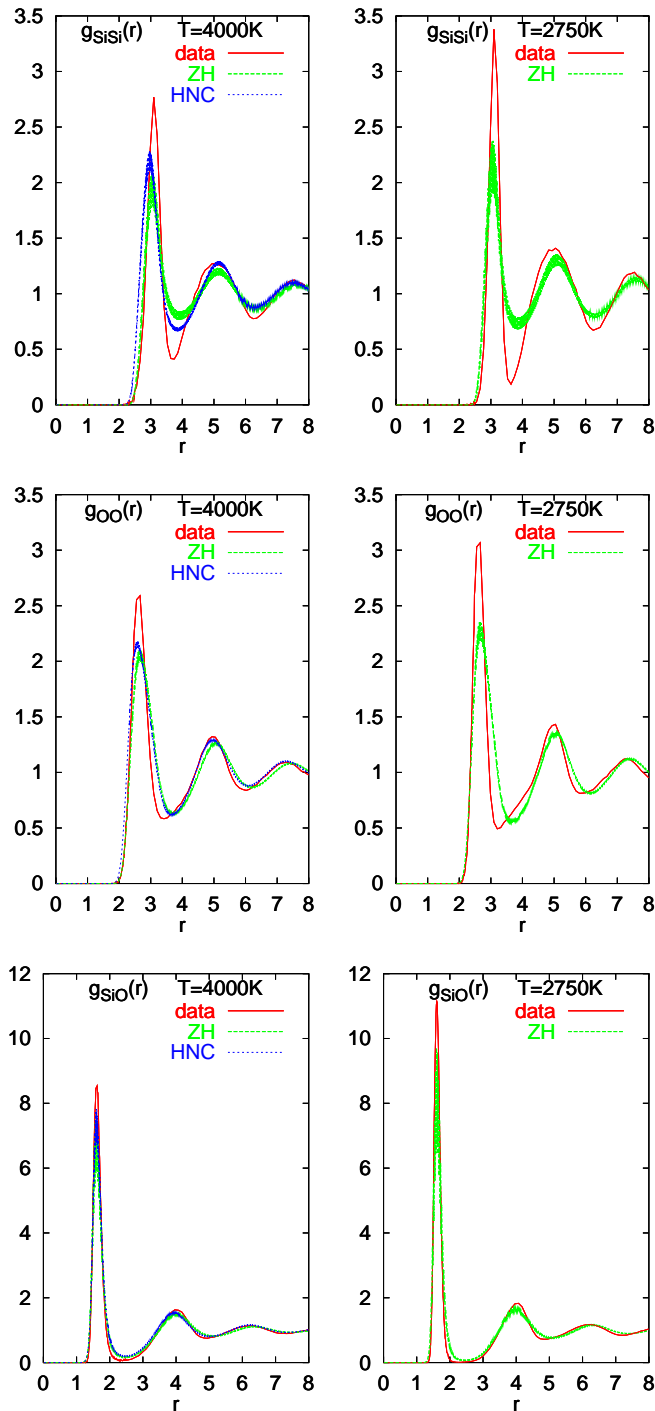
	A (eV)	B (Å ⁻¹)	C (eV · Å ⁻⁶)	α (eV)	σ (Å)
SiSi	0.0	0.0	0.0	1219.45	0.42
OO	4.87318	2.76	175.0	0.0344	2.2
SiO	18003.7572	4.8732	133.5381	1.083	1.31

$$V^{\epsilon\epsilon'}(r) = \frac{Q_{\epsilon\epsilon'}}{r} + A_{\epsilon\epsilon'} e^{-B_{\epsilon\epsilon'} r} - \frac{C_{\epsilon\epsilon'}}{r^6} + v_{sr}^{\epsilon\epsilon'}(r),$$

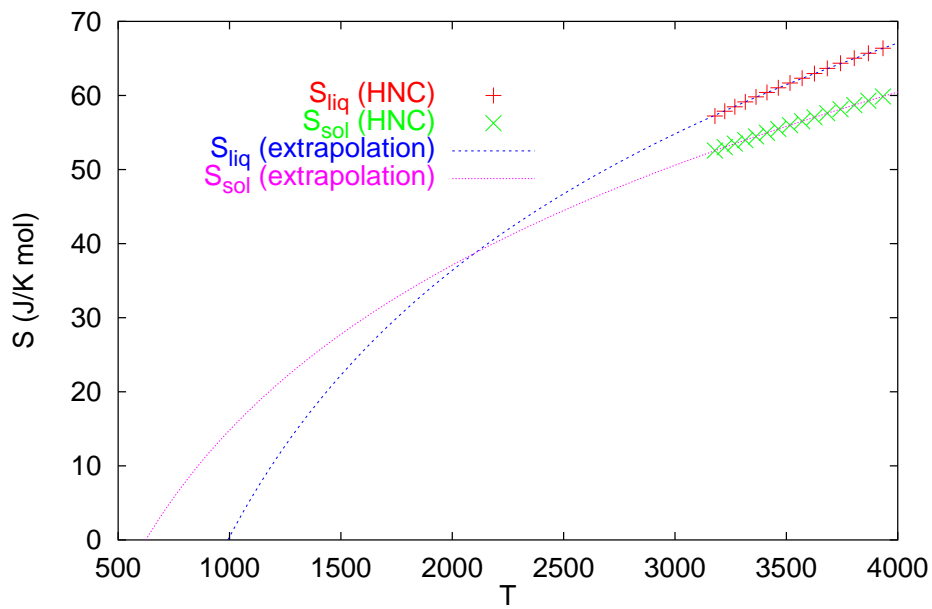
- $Q_{\epsilon\epsilon'} = q_{\epsilon} q_{\epsilon'} e^2$ with $q_{Si} = 2.4$, $q_O = -1.2$
 $e^2 = 1602.19 / (4\pi \cdot 8.8542) \text{ eV} \cdot \text{Å}$.
- $\rho = 0.07083 \text{ Å}^{-3}$, close to the experimental density.
- $v_{sr}^{\epsilon\epsilon'} = 4\alpha_{\epsilon\epsilon'} ((\sigma_{\epsilon\epsilon'}/r)^{24} - (\sigma_{\epsilon\epsilon'}/r)^6)$.
- $T_0 \simeq 2525K$.
- $T_D \simeq 3300K$.
- By taking into account only data at the **lower temperatures available**, the **Arrhenius** behaviour seems to be recovered.
- Very recent numerical results support the hypothesis of a **fragile to strong** transition (Saika-Voivod, Poole and Sciortino, *Nature* **412**, 514 (2001)).

Results

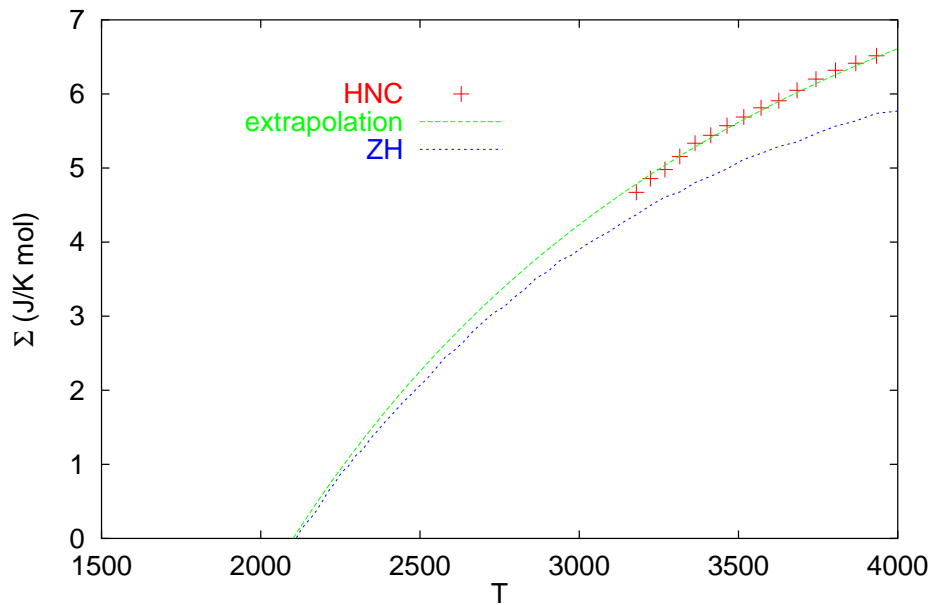
(Coluzzi and Verrocchio, cond-mat/0108464)



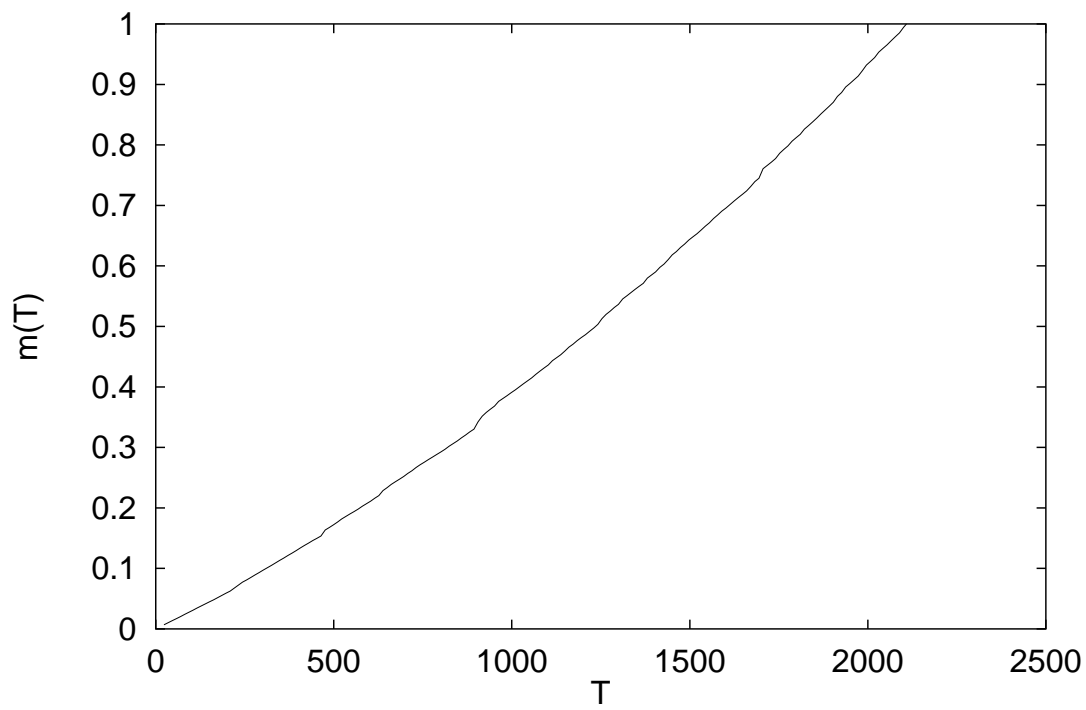
The **analytical** two point correlation functions as obtained within the **HNC** and **ZH** approach compared with **numerical data** by Horbach and Kob (*Phys. Rev. B* **60**, 3169 (1999)) at $T = 4000\text{K}$, 2750K respectively.



The **liquid** and **solid** entropies as obtained by extrapolating HNC results with functions $a_{liq} + b_{liq}T^{-2/5}$ and $a_{sol} + b_{sol} \log T$ respectively.



The **complexity** as obtained by extrapolating analytical results when using **HNC** for liquid quantities and the one within the **ZH** scheme.



Conclusions

- This approach works well for a **Lennard Jones binary mixture**, giving results in agreement with simulations.
- In the **BKS model** we find $T_K \simeq 2100K$, a value larger than the experimental glass transition temperature $T_g \simeq 1446K$ of silica.
- Our findings are compatible with a previously obtained numerical evaluation of $T_0 \simeq 2525K$.
- These analytical results suggest therefore a **failure** of the **BKS model** in capturing low temperature **experimental** properties of **SiO₂**.
- Nevertheless, in a very recent numerical study on the **energy landscape** properties of the model, the hypothesis of a **fragile** to **strong** transition is related to a change in the **complexity** behaviour at $T_D \simeq 3300 K$.
- At low temperatures the **liquid** entropy seems to be not in agreement with a behaviour $\propto T^{-2/5}$.
- The discrepancy could be related to small differences between the model we studied **analytically** and the one which is considered **numerically**.
- On the other hand, the **simple liquid approximations** we used do not give $g(r)$ very similar to the numerical ones in this case.
- Moreover they do not describe precisely enough **high order** correlation functions that could be particularly relevant for **silica**.
- Further both analytical and numerical studies would be required in order to **clarify** the behaviour of this model and its **relevance** for describing experimental silica.