Glass Crossover of Super-Cooled Liquids

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- The glass problem: the dramatic increase upon cooling of the relaxation time of super-cooled liquids
- Mode-Coupling-Theory, ('80) captures many important features of the problem, in particular the two-step nature of the relaxation *but* predicts a glass transition at too high temperatures
- Structural-Glass/Spin-Glass analogy: (Kirkpatrick-Thirumalay-Wolynes, 87-89): p-spin-glass models with ($p > 2$) obey the same dynamical equations.
- Structural-Glass/Spin-Glass analogy: (Kirkpatrick-Thirumalay-Wolynes) : at T_{MCT} the phase space is split into an exponential number of states, disappearance of the transition through nucleation arguments.
- In Spin-glass models the transition occurring at T_{MCT} has the features of a second order phase transition (diverging correlation length and fluctuations) and these features can be also obtained directly in the MCT framework
- Recently (2010-) it has been discovered that the critical properties of the theory are related to those of the Random field Ising model: unexeptected but solid connections.

- The problem: Why and how the dynamical singularity of Mode-Coupling-theory (MCT) becomes a crossover?
- The dynamical singularity at T_{MCT} is assumed to be a genuine second order phase transition and *dynamical* field theoretical methods are applied to it.
- The procedure leads instead to a rather intuitive dynamical model (Stochastic Beta Relaxation) that predicts that the transition is changed into a dynamical crossover.

T. Rizzo, arXiv:1307.4303, EPL 2014

Solution of Stochastic-Beta-Relaxation equations in 3D

- Above T_{MCT}: power-law increase of dynamical fluctuations and dynamical correlation length, scale invariance.
- Near T_{MCT}: (i) Dynamical arrest is avoided (ii) relaxation time grows much faster, from power-law to eponential.
- The structure of fluctuations also displays a qualitative change below T_{MCT}: rare faster regions dominates the relaxation: Dynamical Heterogenities. Dynamics slows down because these regions are rare not because they are larger.
- Dynamical correlation length decreases and decorrelates from the relaxation time. Decoupling between different observables: Deviations from the Stokes-Einstein relationship.

T. Rizzo & T. Voigtmann, '14

Critical Slow Dynamics in MCT

$$\Phi(k,t) = f(k) + G(t)\,\xi_c^R(k) \quad (\beta \text{ regime})$$

$$\sigma = G^2(t)\,(1-\lambda) + \int_0^t (G(t-s) - G(t))\dot{G}(s)ds$$

$$\sigma \propto T_{MCT} - T,\ \sigma \propto \rho - \rho_{MCT}$$

$$\lim_{t\to\infty} G(t) = -B(\sigma)t^b \quad \text{for } \sigma < 0 \text{ (liquid)}$$

$$\lim_{t\to\infty} G(t) = \sqrt{\sigma/(1-\lambda)} \quad \text{for } \sigma > 0 \text{ (glass)}$$

$$\lambda = \frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = \frac{\Gamma^2(1+b)}{\Gamma(1+2b)}$$

- scaling limit: $|\sigma| \ll 1$, $|G(t)| \ll 1$, $1 \ll t = O(\tau_\beta) \ll \tau_\alpha$;

$$\tau_\alpha \propto B(\sigma)^{-1/b}$$

Stochastic Beta Relaxation

- Stochastic β-relaxation (SBR) equation: Extension of the MCT equation for the critical correlator with random fluctuations of the separation parameter.

$$\sigma = G^2(t)\,(1-\lambda) + \int_0^t (G(t-s) - G(t))\dot{G}(s)ds \quad \text{(MCT)}$$

$$\downarrow$$

$$\sigma + s(x) = -\nabla^2\, g(x,t) + (1-\lambda)\, g^2(x,t) + \int_0^t (g(x,t-s) - g(x,t))\frac{dg}{ds}(x,s)ds$$

$$[s(x)s(y)] = \Delta\sigma^2\, \delta(x-y)$$

$$G(t) = [\frac{1}{V}\int g(x,t)dx]$$

T. Rizzo, arXiv:1307.4303, EPL 2014

The replicated Field Theory

$$\mathcal{L} = \frac{1}{2}\int dx \left(-\tau \sum_{ab} \phi_{ab} + \frac{1}{2}\sum_{ab} (\nabla \phi_{ab})^2 + m_2 \sum_{abc} \phi_{ab}\phi_{ac} + m_3 \sum_{abcd} \phi_{ab}\phi_{cd} + \right.$$
$$\left. -\frac{1}{6} w_1 \sum_{abc} \phi_{ab}\phi_{bc}\phi_{ca} - \frac{1}{6} w_2 \sum_{ab} \phi_{ab}^3 \right)$$

- It is possible to resum the loop expansion unveiling a mapping to a quadratic equation in a random field
- This allows to identify non-perturbative effects that show that the glassy phase is not stable: the singularity at T_c is avoided.
- Non-trivial features: (i) typically loop expansions are limited to few orders, here we have control at all orders, similar to the RFIM (ii) but the mapping seems natural in the RFIM model while there is no quenched random field in this case

S. Franz, G. Parisi, F. Ricci-Tersenghi, and T. Rizzo, Eur. Phys. J. E, 34, 102, (2011).

From Replicas to MCT Dynamics

- One can formulate the dynamics in such a way that the dynamical field theory is precisely the *same* of the Replicated theory (essentially different replicas are equivalent to different times).

$$\tau = (w_1 - w_2)\,\phi^2(t) + w_1 \int_0^t (\phi(t-y) - \phi(t))\dot{\phi}(y)dy$$

$$\lambda = \frac{w_2}{w_1}\ .$$

G. Parisi and T. Rizzo, Phys. Rev. E 87, 012101 (2013). F. Caltagirone, U. Ferrari, L. Leuzzi, G. Parisi, F. Ricci-Tersenghi, T. Rizzo, Phys. Rev. Lett. 108, 085702 (2012)

The B-Profile

- At any value of σ, the solution $g(x,t)$ goes at large times as $-B(x)t^b$, *i.e.* all regions of space are liquid.
- SBR equations induce a mapping between the realisation of the random temperatures $s(x)$ and a positive function $B(x)$, such a mapping is not possible in the static treatment.
- the B-profile allows a compact description of dynamical quantities like the α-relaxation time, the diffusion coefficient and the correlation length.

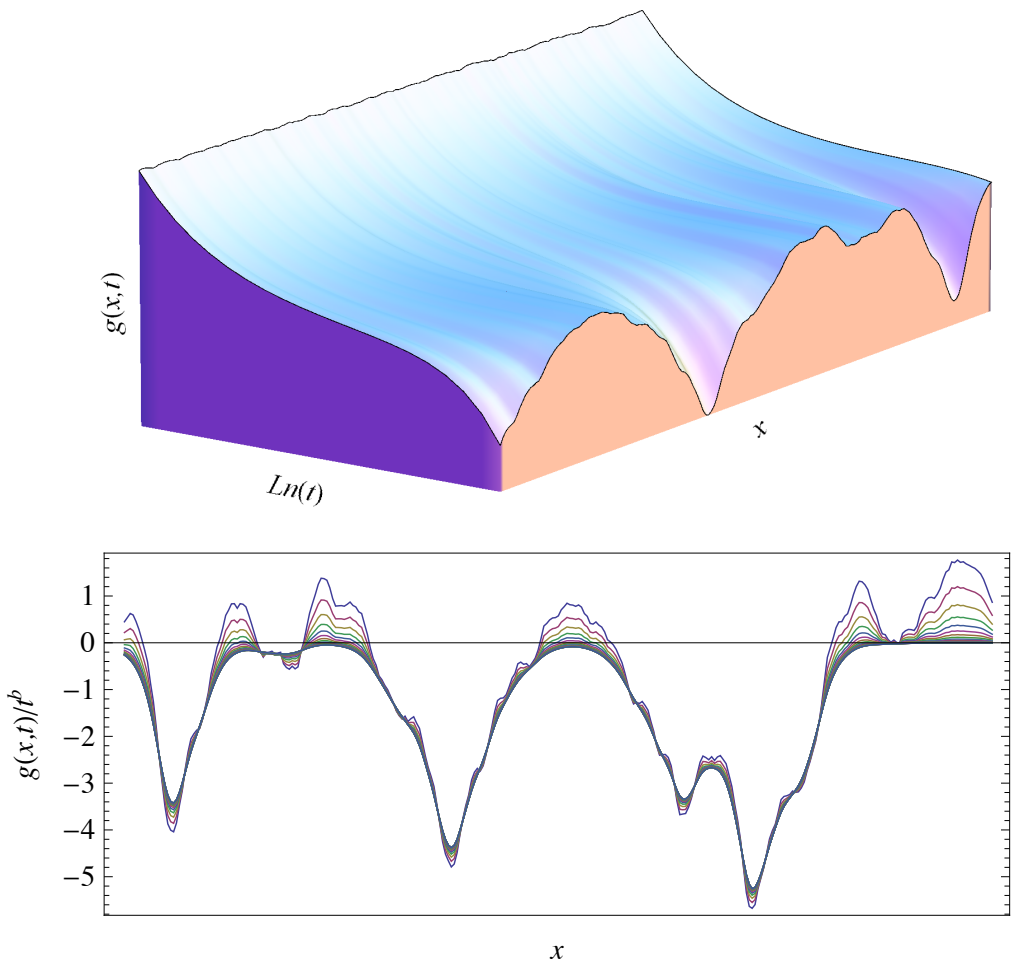

Figure 1: Top: Pictorial representation of the solution of SBR equations in finite dimension for a given realisation of the random $\sigma(x)$. (generated from actual solution of a 1D system). At large times the solution converges to the form $-B(x)t^b$, thus inducing a mapping between the realisation of the random $\sigma(x)$ and a positive function $B(x)$, the B-profile. Bottom: Plot of $g(x,t)/t^b$ vs. x for increasing times t: increasing the time the curves converge to the B-profile.

Viscosity and Diffusivity

$$\eta = \tau_\alpha \sim \left(\frac{1}{V} \int B(x)\, dx \right)^{-1/b}$$

$$D \sim \frac{1}{V} \int B^{1/b}(x)\, dx$$

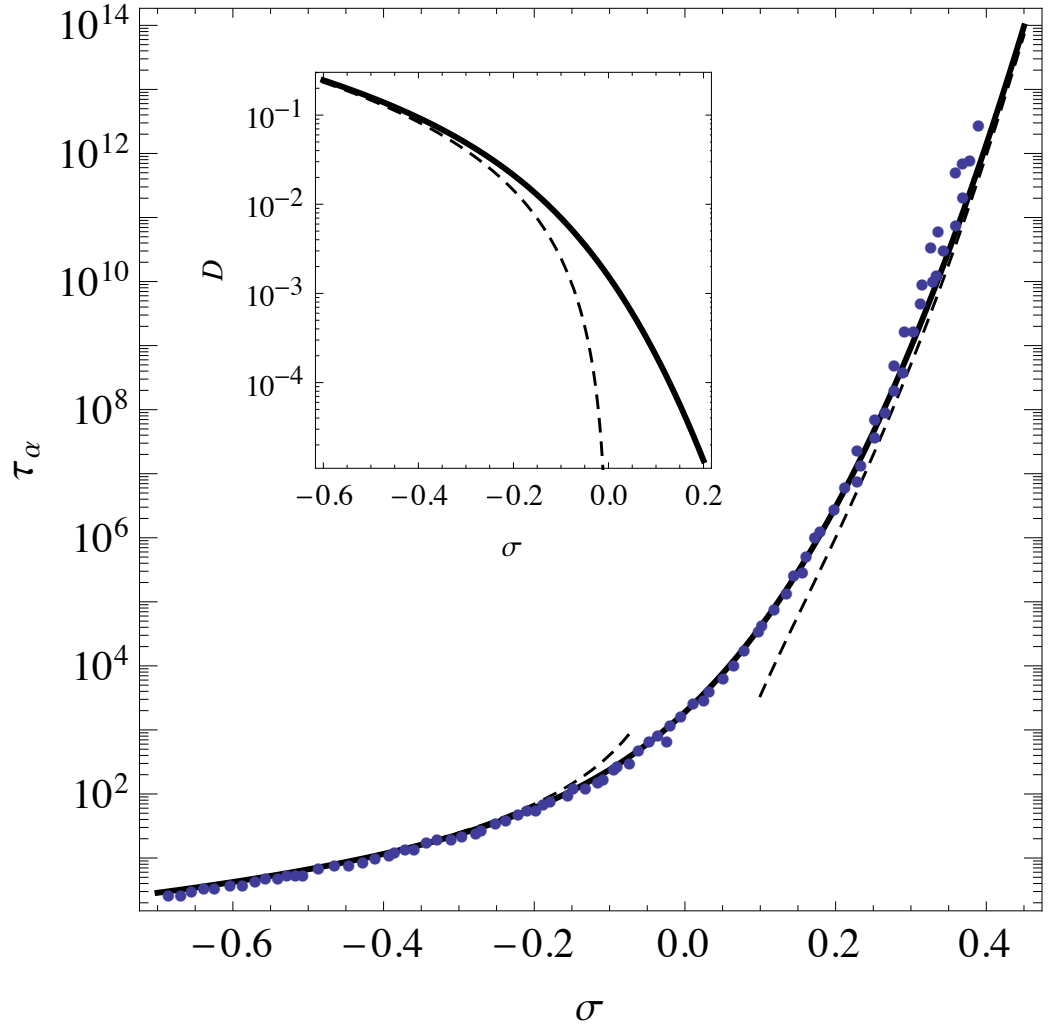

Figure 2: Simplified SBR: plot of the α relaxation time τ_α vs. the separation parameter σ for $\Delta\sigma = .1$ and $\lambda = .75$. The dashed lines correspond to the leading asymptotic behavior. Symbols are dielectric-spectroscopy data for propylene carbonate from Lunkenheimer *et al* (2000). Inset: plot of the Diffusion constant vs. the separation parameter σ for $\Delta\sigma = .1$ and $\lambda = .75$. The dashed line corresponds to the ideal MCT result $D \propto 1/\sigma^\gamma$.

Some Comments

- Dynamical arrest is avoided *and* replaced by a crossover from power-law to exponential
- there is no *ad hoc* assumption on nucleation or activated processes in the derivation, actually the initial assumption is that T_{MCT} marks a genuine phase transition
- could work in an extended range of temperature, even close to T_g
- used as a fit function but the actual computation of the coupling constants is feasible for many systems

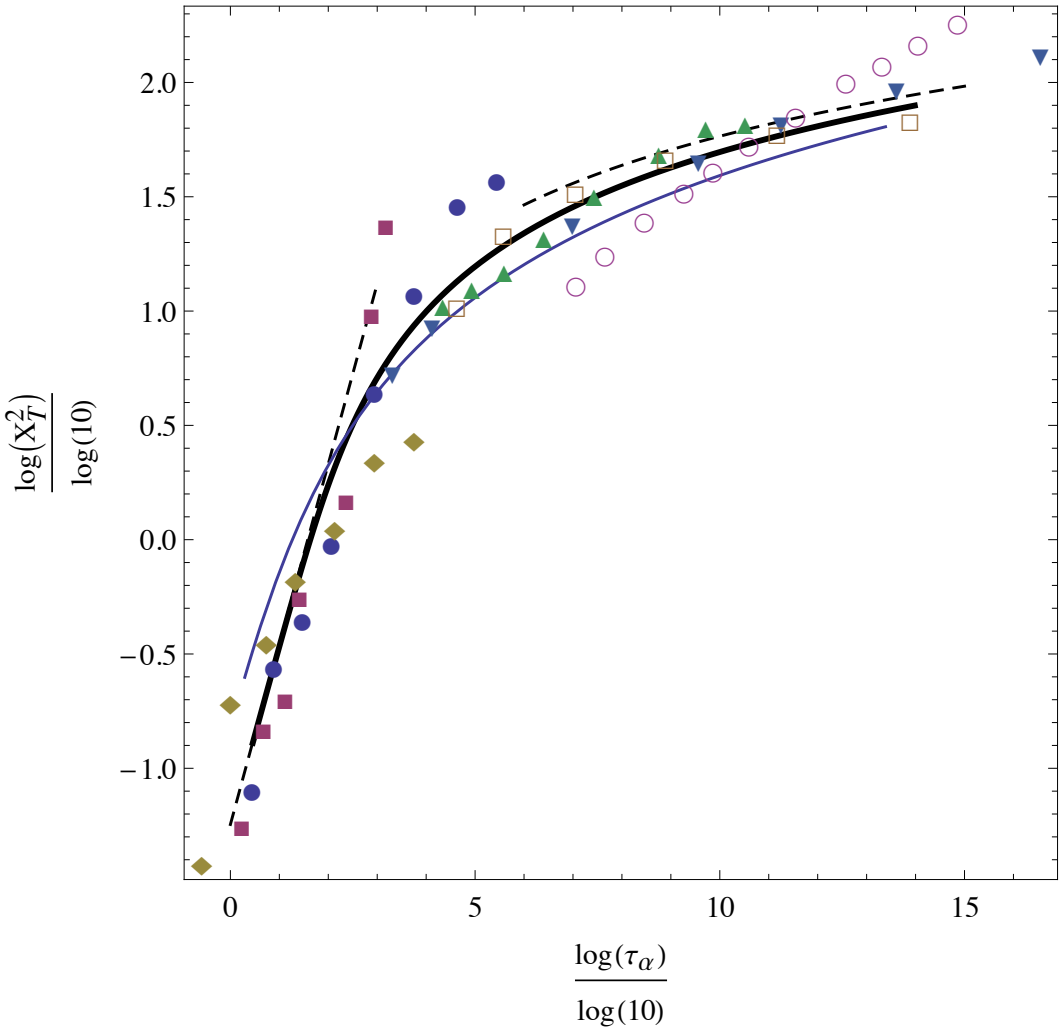

Figure 3: simplified SBR: plot of the squared thermal susceptibility vs. τ_α for $\Delta\sigma = .1$ and $\lambda = .75$. The dashed lines correspond to the asymptotic behaviors. Symbols are experimental data shifted by arbitrary factors along the vertical *C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L'Hote, and G. Tarjus, Phys. Rev. E 76, 041510 (2007).* (circles: Lennard Jones mixture; squares: hard spheres; BKS silica: diamonds; triangles: propylene carbonate; inverted triangles: glycerol; open circles: OTP; open squares: salol). The thin solid line is the expression proposed in the same paper.

Non-Monotonous Correlation Length

$$\Gamma(r) = \frac{1}{V} \int B(x) B(x+r)\, dx$$

$$\Gamma_n(r) \equiv \frac{\Gamma(r) - \Gamma(\infty)}{\Gamma(0) - \Gamma(\infty)}$$

- $\Gamma_n(r)$ has a bell-shaped form with rapidly decaying tails both below and above $\sigma = 0$
- non-monotonous behavior with σ, appears to be related to recent observations in numerical simulations (Berthier, Kob 2010-)

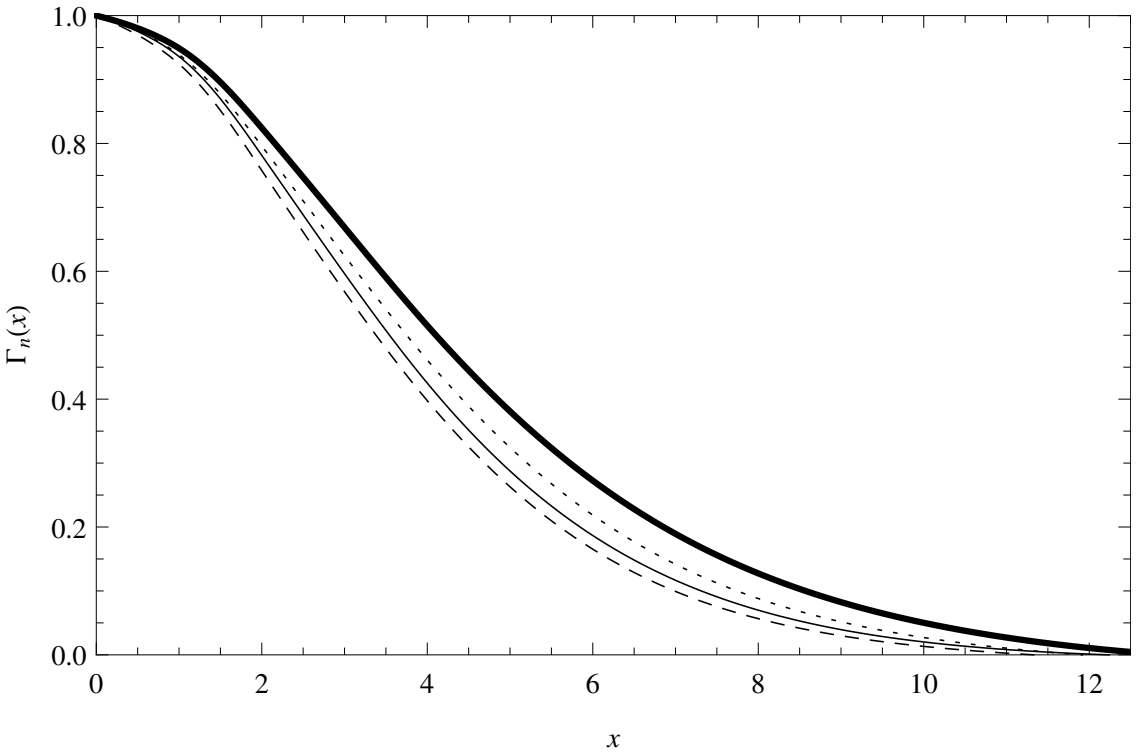

Figure 4: Plot of the normalized autocorrelation of the B profile in 3D for $\sigma = -0.006$, 0, 0.006, 0.012 (dashed, dotted, thick, solid).

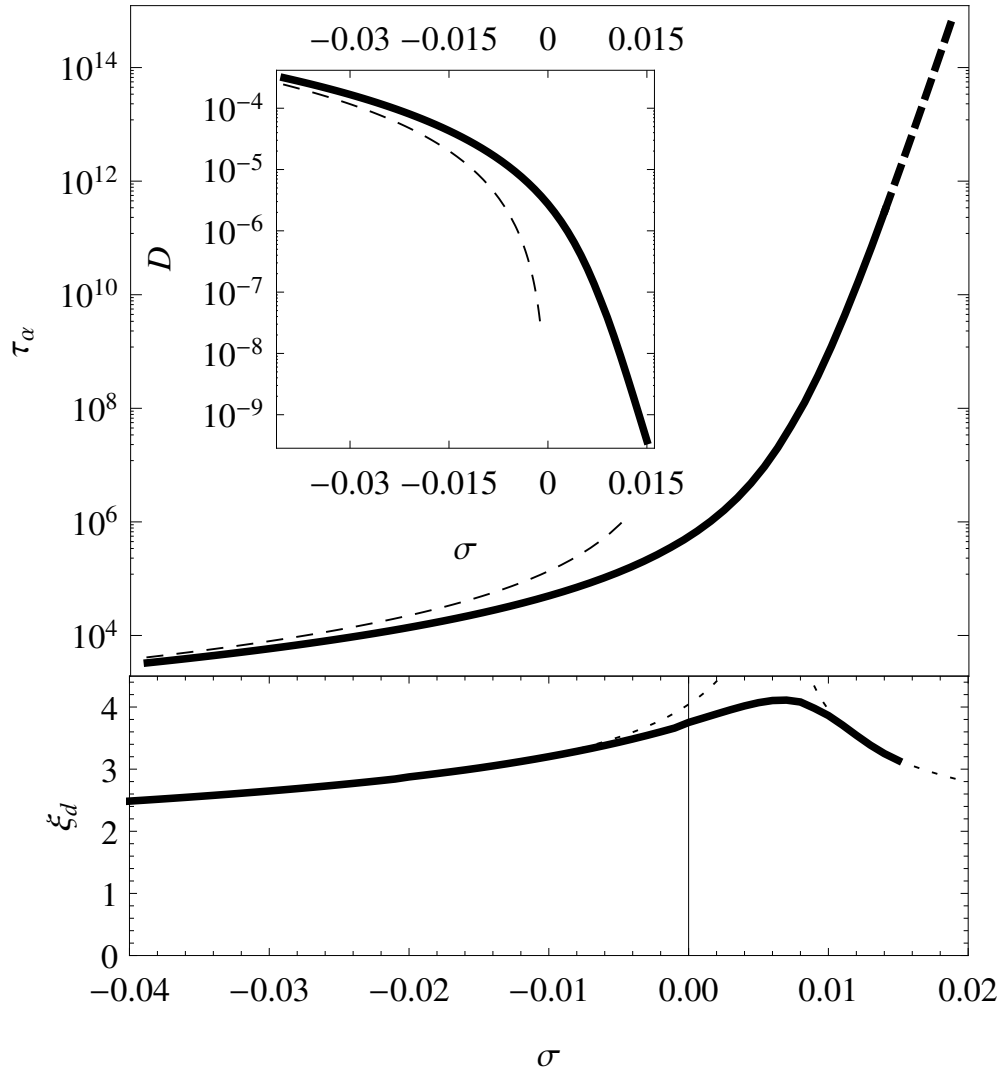

Figure 5: Top: τ_α vs. σ from SBR in 3D. Inset: D vs. σ in 3D. Bottom: The correlation length ξ_d (defined as half-width at half-maximum of $\Gamma(r)$) as a function of σ.

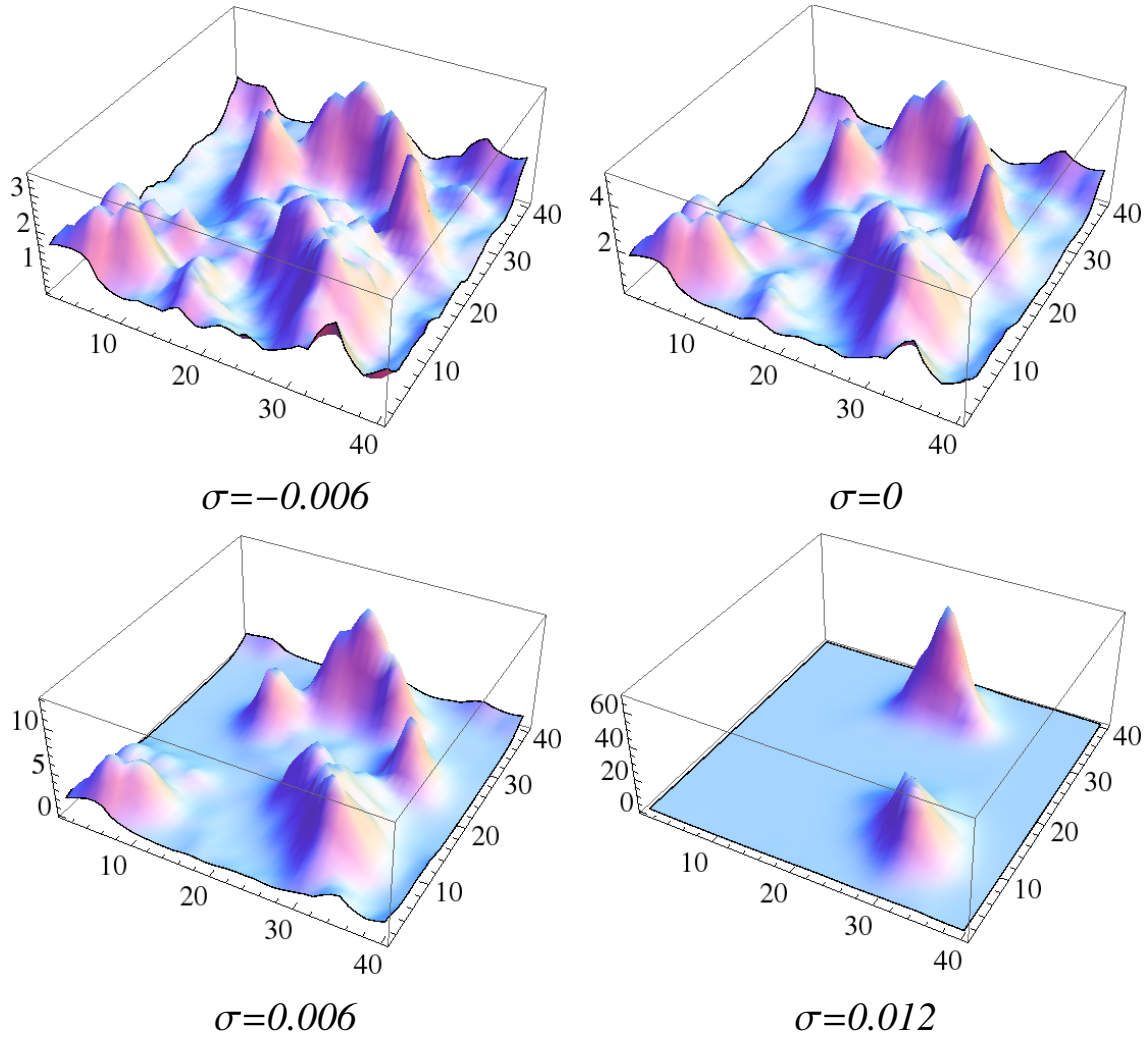

Figure 6: Normalized B-profile $B(x)/\overline{B}$ on a plane sliced from a cubic box for different values of σ.

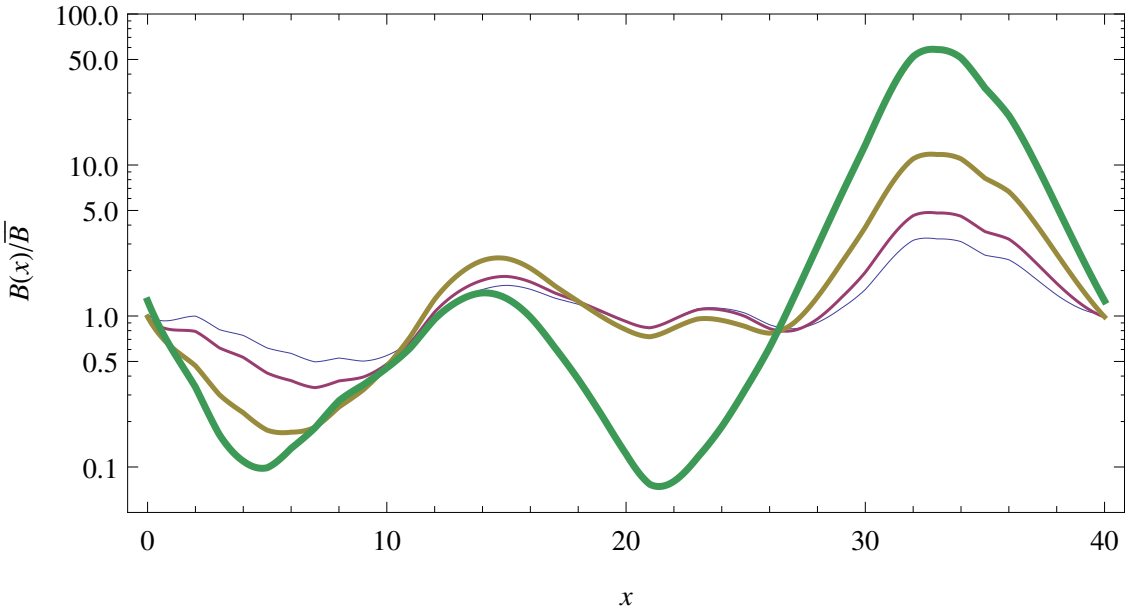

Figure 7: Log-plot of the Normalized B-profile $B(x)/\overline{B}$ on the line $x = 20$ cut from the planes of figures 6 (increasing values of σ correspond to increasing line thickness).

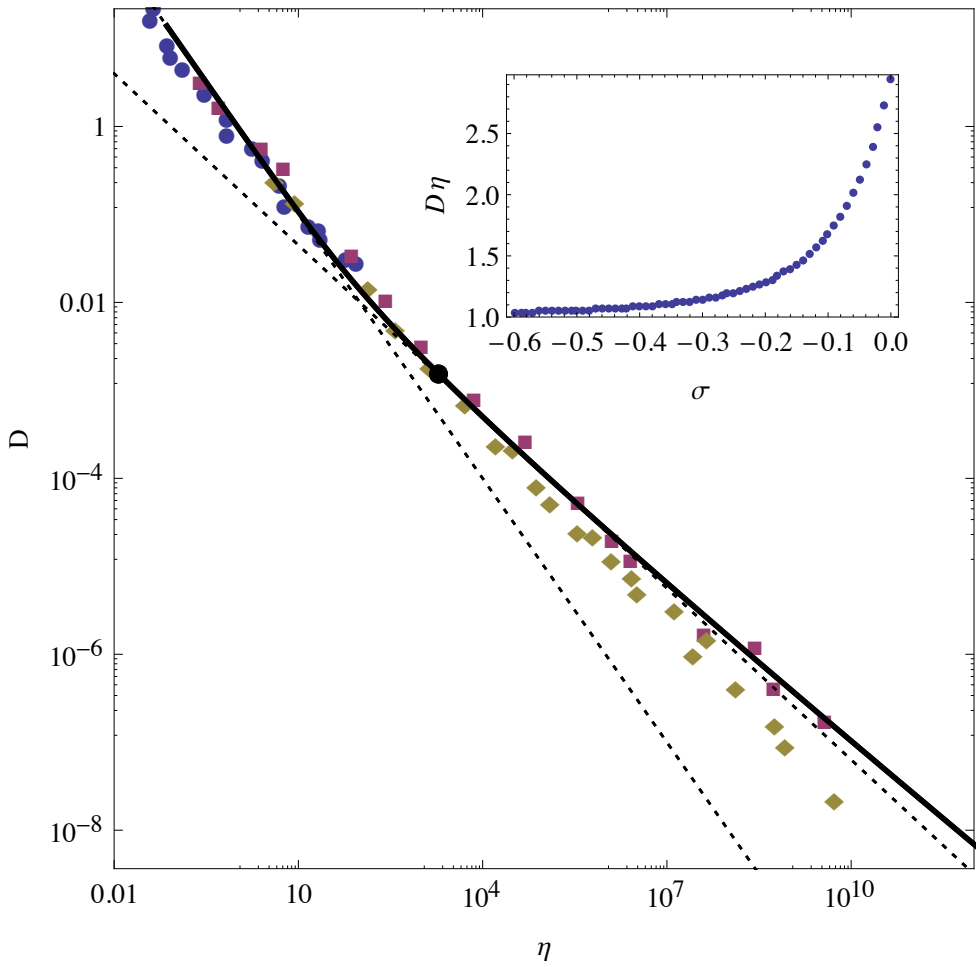

Figure 8: simplified SBR: plot of the Diffusion constant vs. the viscosity for $\Delta\sigma = .1$ and $\lambda = .75$. The straight lines correspond to $D \propto \eta^{-1}$ (the Stokes-Einstein relation) and to a fractional SER $D \propto \eta^{-.65}$. The actual asymptotic behavior is $D \propto \eta^{-b}(\ln \eta)^{\frac{b\gamma-1}{2}}$, the logarithmic prefactor induces a huge correction and as a consequence a fit with a pure fractional SER gives an exponent 0.65 considerably higher than $b = .558$. The point where the SER breaks down (intersection of the straight lines) corresponds to a temperature higher than T_c (dot). Smaller symbols are experimental data for o-terphenyl by Lohfink and Sillescu (1992)(circles: tracer diffusion at $T > T_c$, diffusion of ACR dye, diamonds: diffusion of TTI dye).

Future Directions and Open Problems

- Quantitative tests with actual coupling constants, (length, shift of T_{MCT}, Lennard-Jones vs. HARM crossover sharpness)
- different dimensions and finite-size effects
- better understanding of the α regime
- cannot sustain too large fluctuations and must be abandoned at some point. Conjecture: non-standard activation characterized by elementary events that have intrinsic time and length scales of an unusual large (but not increasing) size (mesoscopic vs. microscopic).
- Connection with configurational complexity phenomenology

Conclusions

- Dynamical Field Theoretical loop corrections to MCT lead to SBR.
- displays a rich phenomenology common to most super cooled liquids.
- displays simultaneously an increase of several orders of magnitude of the relaxation time *and* a decrease of the dynamical correlation length.
- below T_{MCT} there are strong dynamical heterogeneities, crossover from scale-invariance to activated-like, SER deviations.
- None of these qualitative and quantitative features was put *ad hoc* into the model. In particular one should not confuse the fluctuations of the order parameter (the standard starting point of the computation) of the original theory with the fluctuations of the temperature in SBR (the result of the computation).

Thanks!

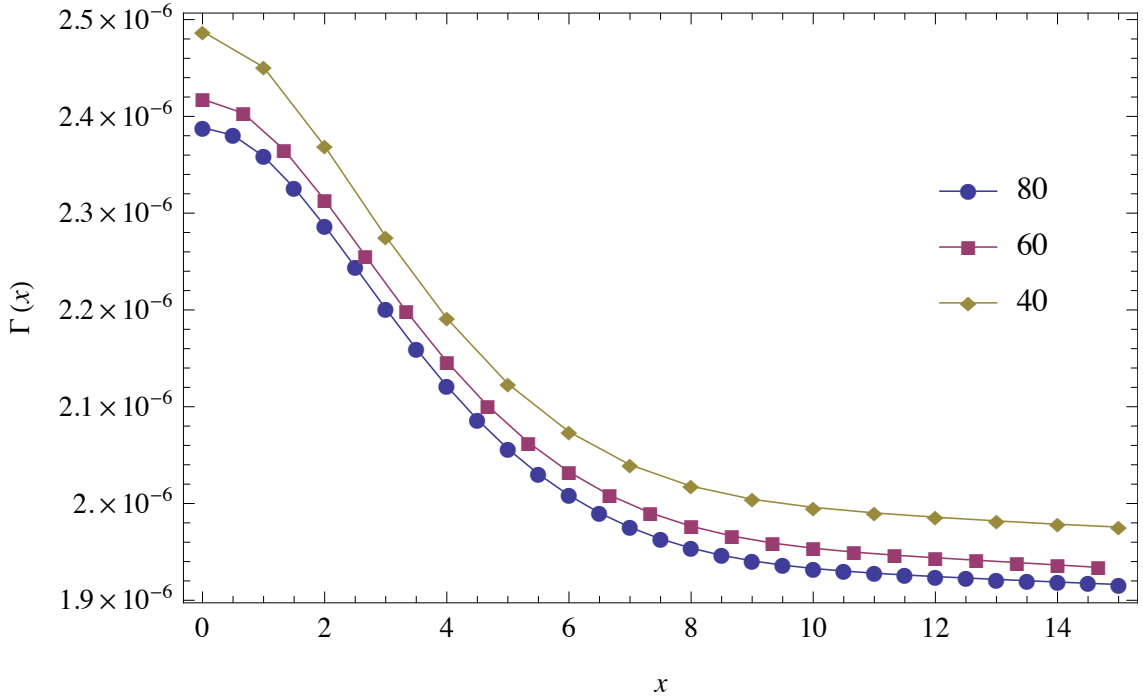

Figure 9: Existence of the continuum limit of the $B(x)$ profile.