Beyond Idealized Mode-Coupling Theory: "Aging", Quantum & Non-Mean-Field Effects In Liquids.

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Mode-Coupling Theory of Relaxation: Case of Supercooled liquids.

Exact equation of motion for intermediate scattering function $F(k,t) = \frac{1}{N}\langle \rho_k(t)\rho_k^*(0)\rangle$

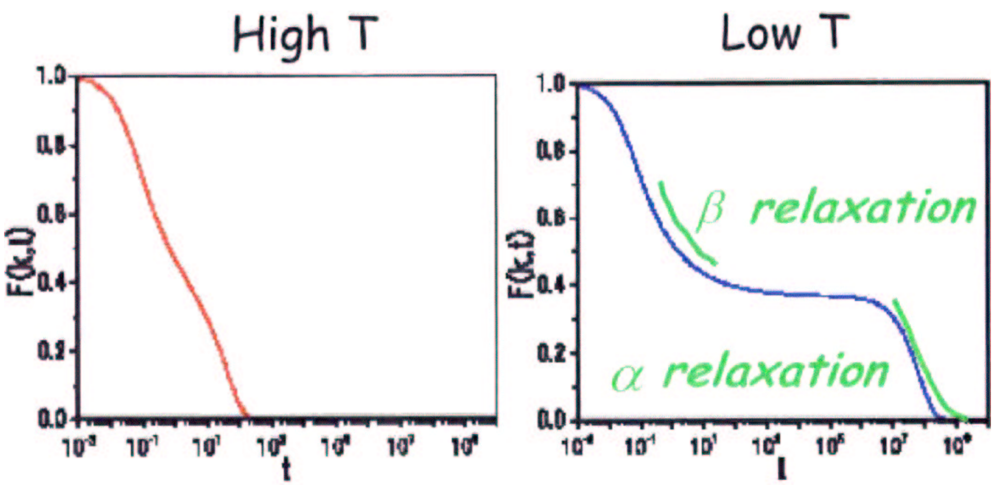
$$\frac{\partial^2 F(k,t)}{\partial t^2} + \frac{k^2 k_B T}{S(k)} F(k,t) + \int_0 dt'\, M(k,t-t') \frac{\partial F(k,t')}{\partial t'} = 0 \qquad \ldots\ldots(1)$$

Mode-Coupling Approximation for M(k,t):

$$M(k,t) \approx \sum_q |V_{q,k-q}|^2 F(q,t) F(|k-q|,t)$$

contains information about fluid structure

Renders (1) closed, to be solved self-consistently. What are the predictions, and how good are these predictions?



- Cage effect, which is included in eq. (1), leads to sequence of relaxation regimes at low T, including power-law (β) and stretched exponential (α). Relaxation at high T is exponential
- At some finite temperature, complete dynamical arrest occurs.
- Various scaling laws are predicted ("factorization" in β-relaxation, "time-temperature superposition" in α-relaxation …)

Successes

- Does reasonable job predicting sequence of relaxation events and various scaling laws.
- Nontrivial predictions made for systems with attractive interactions (multiple glassy states, logarithmic relaxation, …) – verified experimentally.
- Quantitative results for "normal" liquids (classical systems near triple point; transport, neutron scattering, …)

Failures

- Incorrectly predicts location of glass transition (ρ_c or T_c)
- Assymptotic (α-relaxation) behavior may be in error.
- Derived expression results from completely uncontrolled approximations. Mean-field-like character of such approximations suggests relaxation via correlated, heterogeneous motion in liquid is beyond scope of idealized MCT (Activated processes, …)

How is MCT derived ?

- Projected operator method: memory function $M(t) \approx \left\langle \hat{f}_k e^{iQLt} \hat{f}_{-k} \right\rangle$ noting that $f_k \sim \sum_q f_{k-q,q} \rho_{k-q} \rho_q$ project onto subspace of bilinear density modes, and factorize resulting 4-point density correlations.
- Fluctuating Hydrodynamics: using free energy F

$$F \sim \frac{1}{2m} \int d\vec{r} \, \frac{\vec{J}(\vec{r},t)^2}{\rho(\vec{r},t)} + F'[\rho(\vec{r},t)]$$

with $\frac{\delta F'[\rho]}{\delta \rho} = k_B T \left\{ \ln \rho(\vec{r},t) - \int d\vec{r}' C_2(\vec{r}-\vec{r}') \rho(\vec{r}',t) + \ldots \right\}$

and Hydrodynamic laws (along with factorization of multipoint correlations …)

- Dynamical versions of liquid structure closer (MSA, …)
- Diagrammatic (Field-Theoretic) MSR Approach


(1-loop, no vertex renormalization)

Note: exact for simple spin-glass models (p=3 spherical model …)

How to go beyond idealized classical MCT?

- A quantum MCT for "simple" quantum liquids (quick and dirty)
- Treatment of driven systems (quick and dirty)
- Beyond 1-loop – Treatment of multi-point correlations.

An Idealized Quantum Mode-Coupling Theory

Formulation + Test cases:

Reichman & Rabani, PRL, 87, 265701 (2001)

Rabani et al., PNAS, 99, 1129 (2002)

Rabani & Reichman, J.Chem.Phys. 116, 6271 (2002)

Rabani & Reichman, Europhys.Lett. 60, 656 (2002)

Experiments on p-H_2 and o-D_2

Bermejo et al. PRL, 83, 5354 (2000)

Mukherjee et al. Europhys. Lett. 40, 153 (1997)

Consider simple liquid near triple point, neglect (for now) particle statistics.

Case of liquid p-H_2:

- Potential well parametrized
- Experiments near T=14K show enhanced transport, existence of peaks in S(k,ω) at high |k|… not expected based on classical thinking…

Example: Neutron Scattering

- Starting with variables $\hat{\rho}_{\vec{q}} = \sum_{\alpha=1}^{N} e^{i\vec{q}\hat{r}_\alpha}$ (density operator)

(longitudinal current operator)

$$\hat{j}_{\vec{q}} = \frac{1}{2m|q|}\sum_{\alpha=1}^{N}\left[\left(\vec{q}\cdot\hat{p}_\alpha\right)e^{i\vec{q}\hat{r}_\alpha} + e^{i\vec{q}\hat{r}_\alpha}\left(\hat{p}_\alpha\cdot\vec{q}\right)\right]$$

Formulate exact equation for motion

$$\frac{\partial^2 F^k(q,t)}{\partial t^2} + \omega_k^2(q)F^k(q,t) + \int_0^t dt'\, K^k(q,t-t')\frac{\partial F^k(q,t')}{\partial t'} = 0$$

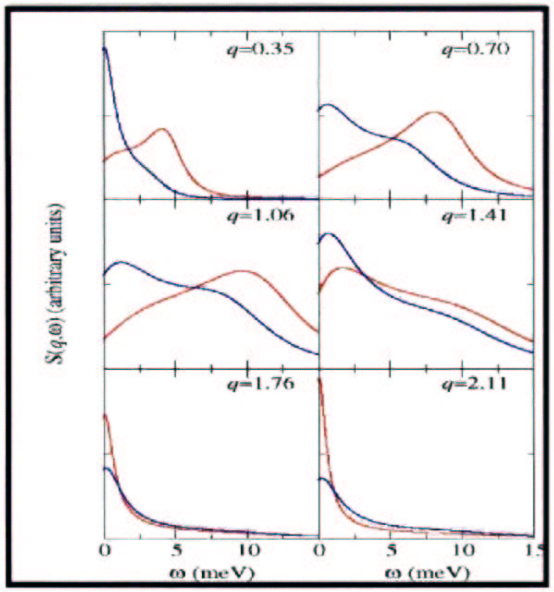
where

$$F^k(q,t) = \frac{1}{\beta\hbar}\int_0^{\beta\hbar} d\lambda \left\langle \hat{\rho}_{\vec{q}}^{+}\hat{\rho}_{\vec{q}}(t+i\lambda\hbar)\right\rangle$$

Mode-Coupling like manipulations may be made to render approximate, closed nonlinear integro-differential equation for $F^k(q,t)$.

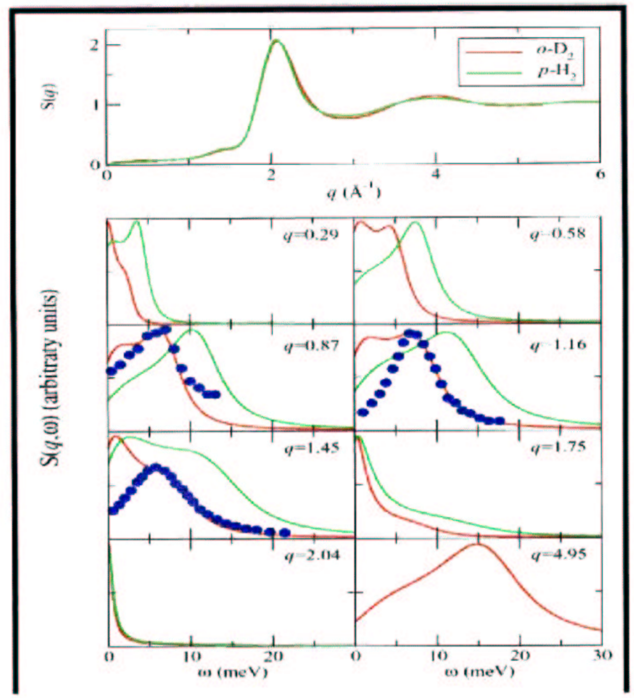
(Numerically) Exact path-integral Monte Carlo is used to generate static correlations necessary as input.

Dynamic Structure Factor: *para*-Hydrogen



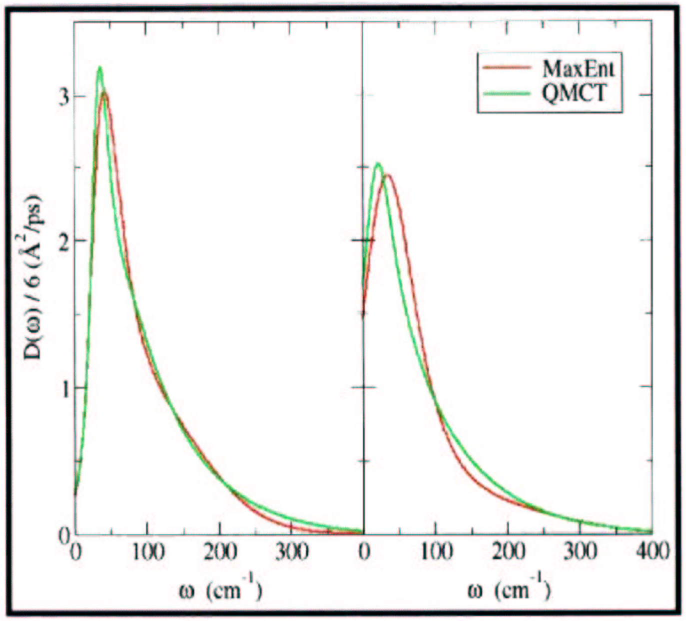
The dynamic structure factor for liquid *p*-H_2 at T = 14K (red curve) and T=25K (blue curve). The coherent density fluctuations give rise to a high intensity peak at finite frequency, that disappears at q = 1.4$Å^{-1}$, in agreement with the experiment. The peak positions and width do show slight differences (5%) from the experiments.

Dynamic Structure Factor: *ortho*-Deuterium



The dynamic structure factor for liquid *p*-H_2 (green curve) and *o*-D_2 (red curve) at T = 20.7K. The coherent oscillations in the intermediate scattering function give rise to a high intensity peak at finite frequency in the dynamic structure factor. Blue solid circles show the experimental results for single excitation collective dynamics of *o*-D_2.

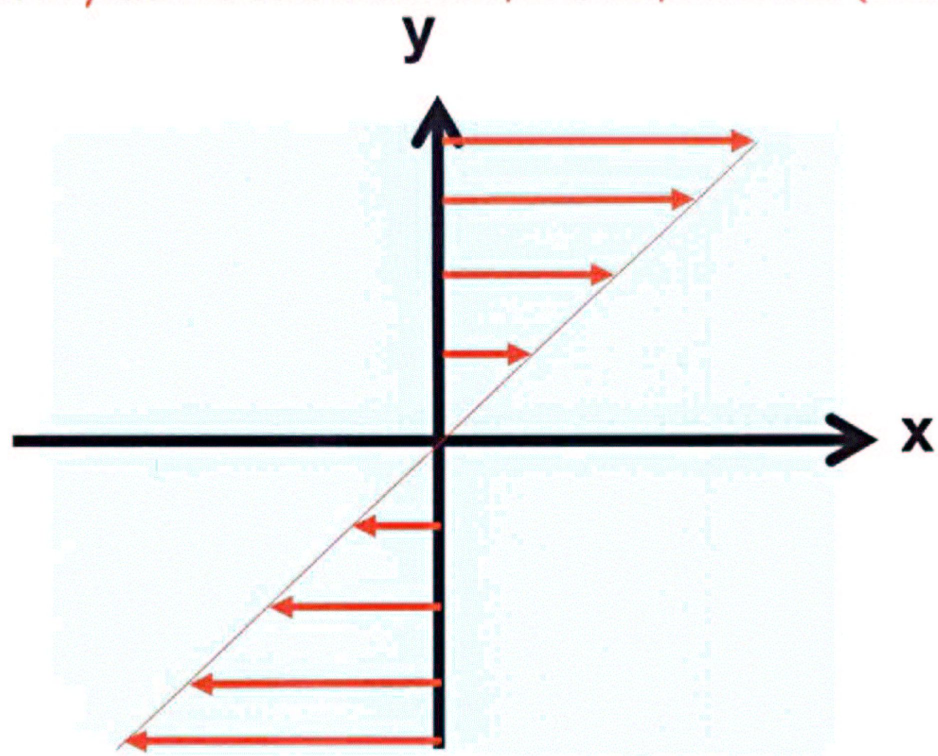
Frequency-Dependent Diffusion Coefficient



$D(\omega)$ calculated from the quantum mode-coupling theory (green curve) and from an analytic continuation of imaginary-time PIMC data (red curve) for liquid p-H_2 at T=14K (lower panel) and T=25K (upper panel). The good agreement between the two methods is a strong support for the accuracy of the quantum mode-coupling approach for liquid p-H_2.

Supercooled Colloidal Suspension Under Shear

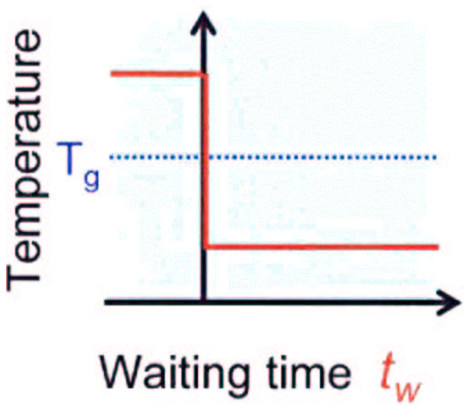
K. Miyazaki & D.R. Reichman, PRE 66, 050501R (2002)

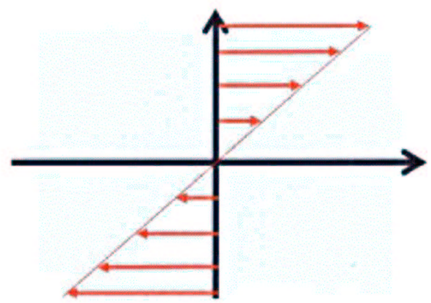


$$v_0(\vec{r}) = (0, \quad \dot{\gamma} x)$$

Analogy with AGING

AGING **SHEAR**





Non-Equilibrium and Non-Stationary

Non-Equilibrium and Stationary

Dependence on the nonequilibrium parameters

The density correlation function

$$F(k,t) = \langle \rho_k(t+t_{\mathrm{w}})\rho_{-k}(t_{\mathrm{w}}) \rangle$$

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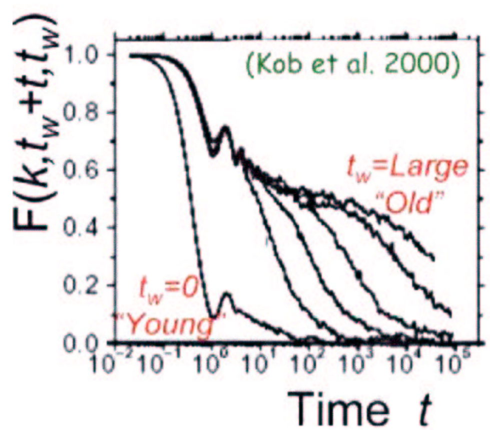
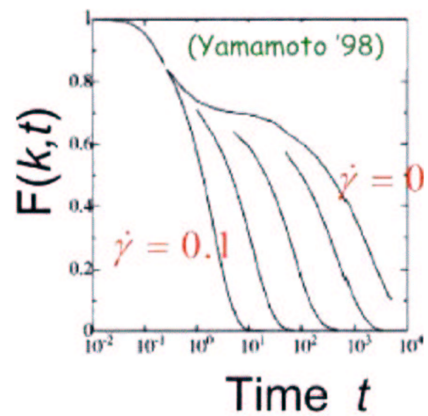




$$t_w \Longleftrightarrow \dot\gamma^{-1}$$

Under Shear

Generalized diffusion equation

$$\frac{\partial \rho(r)}{\partial t} + v_0(r)\cdot\nabla\rho(r) = D\nabla\left[\nabla\rho(r) - \rho(r)\nabla\int dr' c(r-r')\delta\rho(r')\right]$$

Convection term! $v_0(r) = (0, \dot{\gamma} x)$

MCT equation

$$\frac{\partial F(k,t)}{\partial t} + k_x\dot{\gamma}\frac{\partial}{\partial k_y}F(k,t) = -\frac{Dk^2}{S(k)}F(k,t) - \int_0 dt' M(k,t-t')\frac{\partial F(k,t')}{\partial t'}$$

Convection term!

With Memory Function

Time dependent wavevector $\vec{k}(t) = \exp[\dot{\gamma} t]\cdot\vec{k}$

$$M(k,t) = \frac{\rho_0 D}{2}\int d\vec{q}\left[V(k,q)V(k(t),q(t))F(q(t),t)F(k(t)-q(t),t)\right]$$

$$V(k,q) = \hat{k}\cdot\left\{\vec{q}c(q) + (\vec{k}-\vec{q})c(k-q)\right\}$$

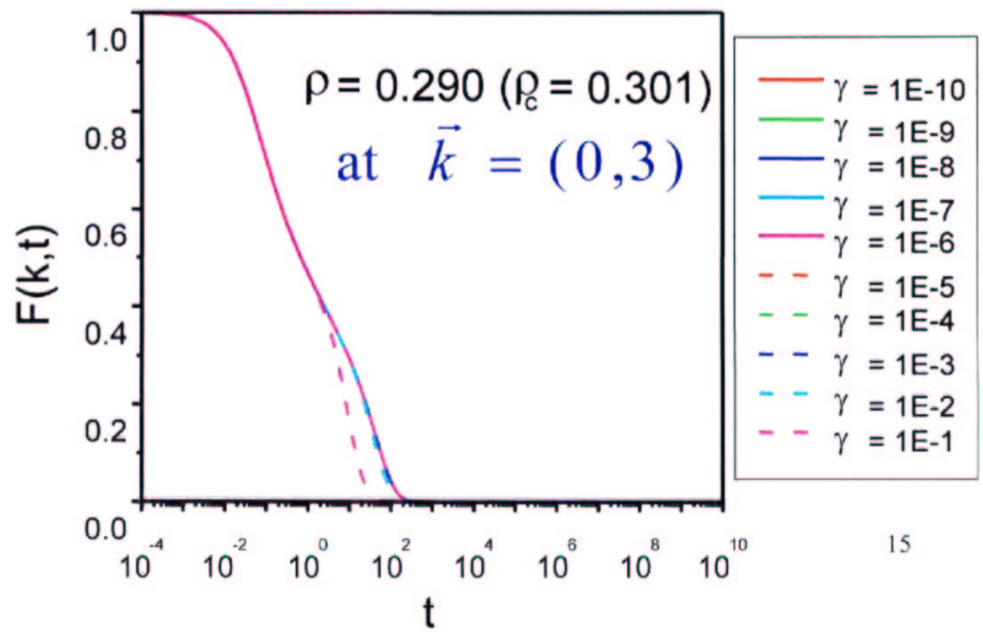
Results

Due to a purely technical difficulty, we treat

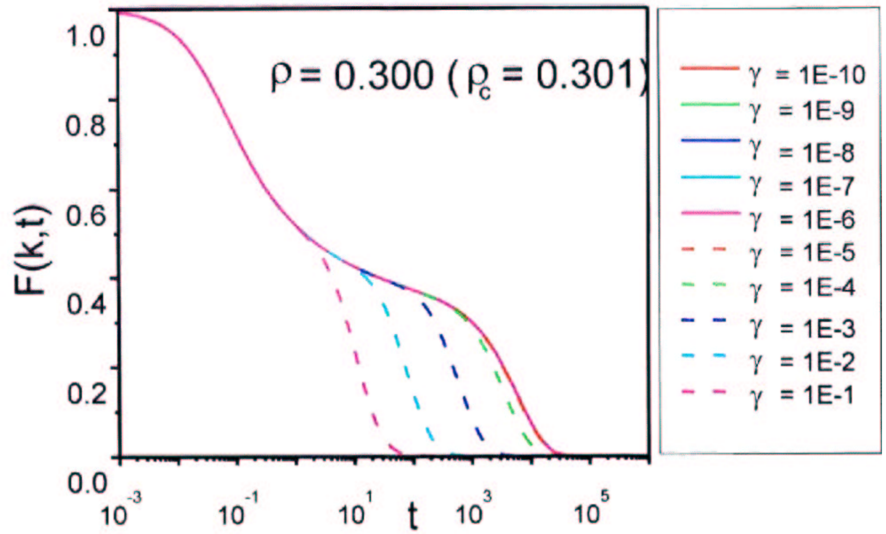
- 2-dimension colloidal suspension
- Artificially smoothed S(k)

(a) Dynamics of F(k,t)

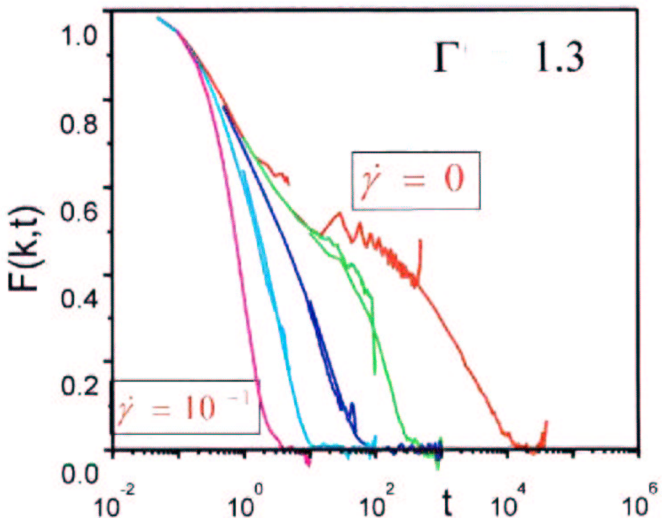
$\rho \ll \rho_c \quad (T \gg T_c)$



$\rho \le \rho_c (T \ge T_c)$



Simulation for 2-d soft-core & binary liquid + $T \ge T_g$



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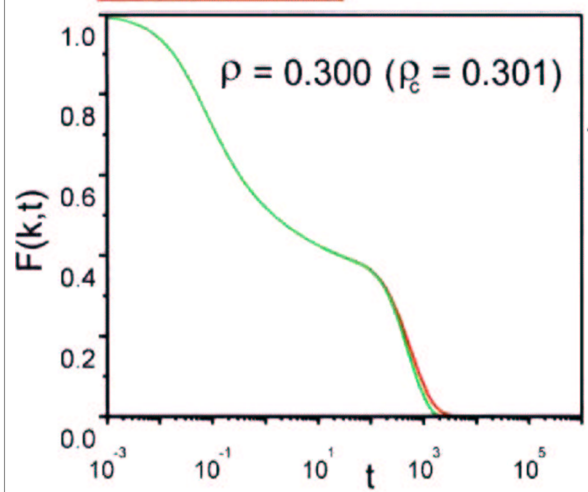
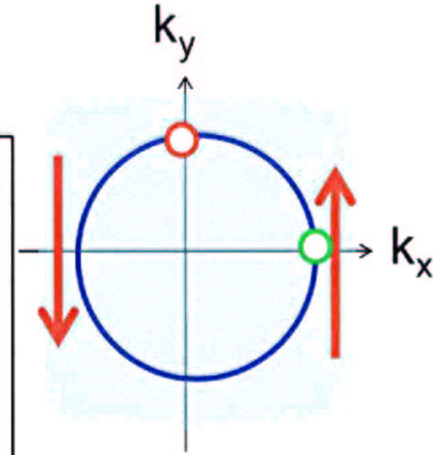
How about anisotropy??

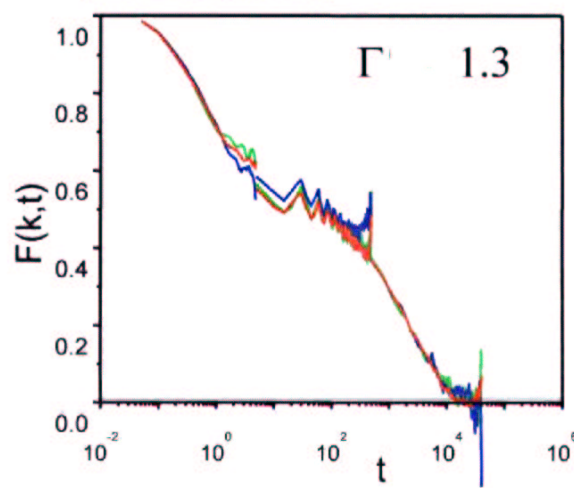
Change the observing points.

MCT





Simulation



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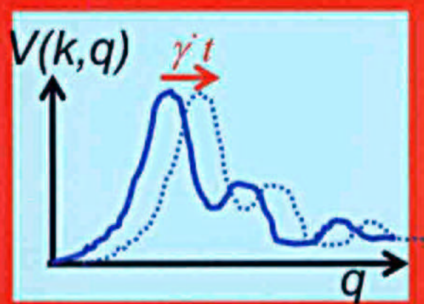
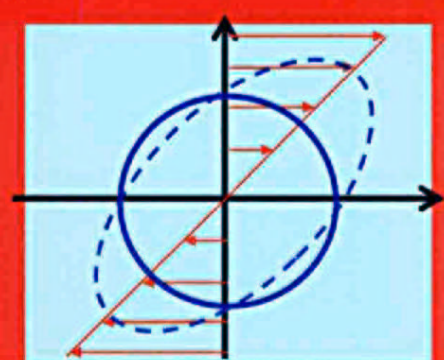
Q: Why is the dynamics is almost isotropic and still it is so drastically disturbed by an minute amount of anisotropic purturbation???

A: A "dephasing" of time-dependent vertex *V(k(t),q(t))* destroys the dynamical arrest of particles!

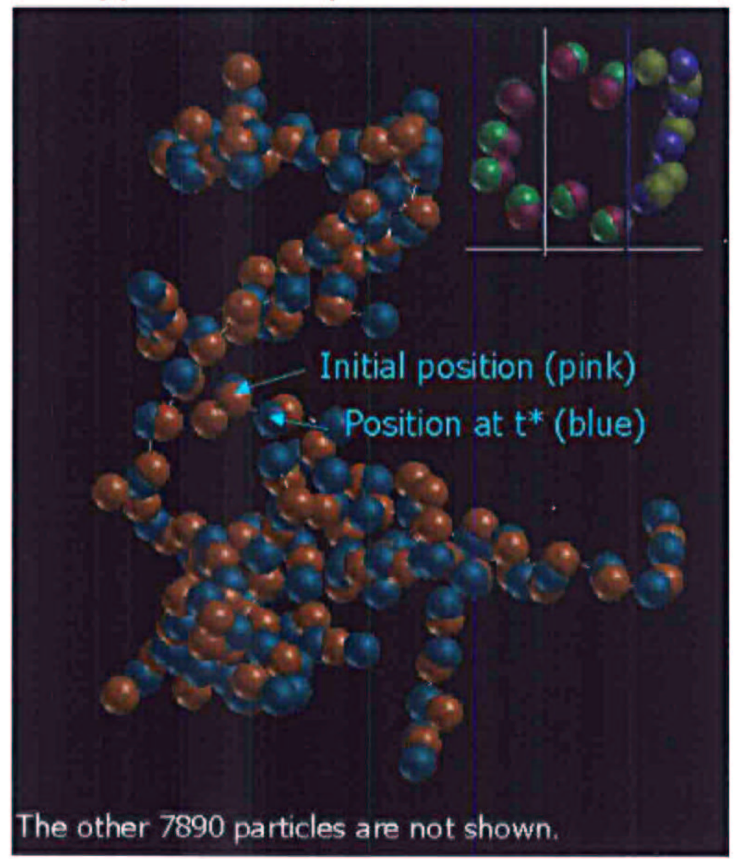


It is completely different from what you see in polymers and critical phenomena under shear, where the distortion of *c(k)* is the dominant cause.



Mode-Coupling Beyond 1-loop

- Dynamic Heterogeneity: At temperatures above T_g relaxation occurs via collective motion of spatially correlated particles: mobile regions.
- Idealized MCT is a mean-field-like theory, cannot capture this behavior



Development of a Mode-Coupling Theory that goes beyond mean-field (1-loop)

- Want: formally exact theory for liquid dynamics not based on path-integral representation of fluctuating hydrodynamics.
- N-ordering approach (Machta & Oppenheim Physica A, 112, 361 (1982))

(a) Construct Orthogonal (infinite) basis of slow modes:

$$Q_0 = 1$$

$$Q_1(\vec{r}) = A(\vec{r}) - \langle A(\vec{r}) \rangle$$

$$Q_2(\vec{r}) = Q_1(\vec{r})Q_1(\vec{r}\,') - \langle Q_1(\vec{r})Q_1(\vec{r}\,') \rangle$$

$$- \langle Q_1(\vec{r})Q_1(\vec{r}\,')Q_1(\vec{r}_1) \rangle * \langle Q_1(\vec{r})Q_1(\vec{r}\,') \rangle^{-1} * Q_1(\vec{r}_2)$$

$$\vdots$$

(b) If system does not have a diverging correlation length (dynamics or static), can use cumulant expansion, express all moments in terms of cumulants, and order cumulants in terms of system size.

(c) Can now express (formally) infinite series closed expression for correlations in terms of multipoint statics and 2-point dynamics. Ordering ~ VK_c^3 (not small, O(1)!).

Example: Memory function for F(k,t) can be expressed M(k,t) =

Static correlations

$$\sum_{|\gamma|=2}^{\infty} X_{\alpha\gamma} * G_{\gamma\gamma'} \cdot X_{\gamma' b} + \sum_{|\gamma|=2}^{\infty} \sum_{|\delta|=2}^{\infty} X_{\alpha\gamma} * G_{\gamma\gamma'} \cdot X_{\gamma'\delta} * G_{\delta\delta'} \cdot X_{\delta' b} + \ldots$$

Mode order

Dynamical propagators

For $|\gamma| = 2$; this term yields the 1-loop, idealized MCT!

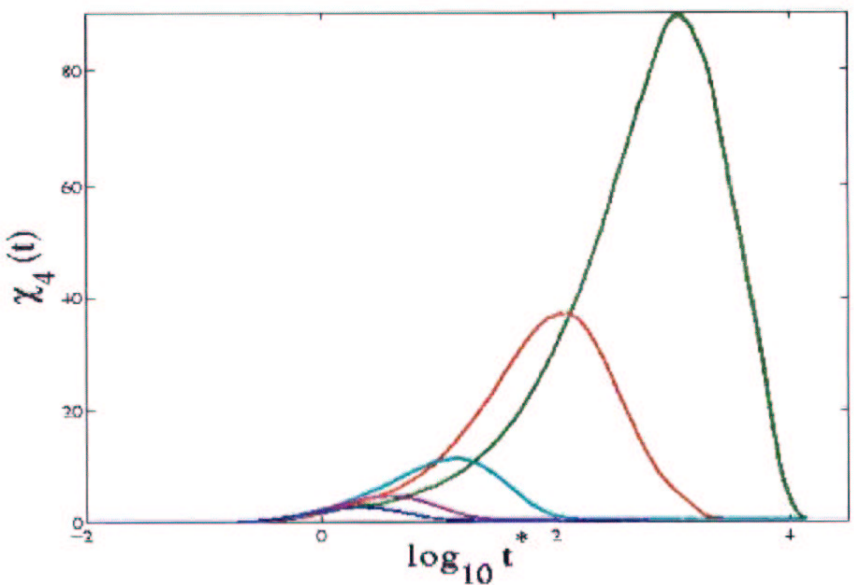
Now, consider non-linear susceptibility

$$\chi_4(t) = \frac{\beta V}{N^2} \int dr_1 \cdots dr_4 W(|r_1 - r_2|) W(|r_3 - r_4|) G_4(r_1 \ldots r_4; t)$$

where

$$G_4(r_1 \ldots r_4; t) = \langle \rho(r_1,0)\rho(r_2,t)\rho(r_3,0)\rho(r_4,t)\rangle - \langle \rho(r_1,0)\rho(r_2,t)\rangle\langle \rho(r_3,0)\rho(r_4,t)\rangle$$

- Tells about growing time and length scales associated with dynamical heterogeneity in supercooled liquids.
- All interesting terms occur beyond 1-loop



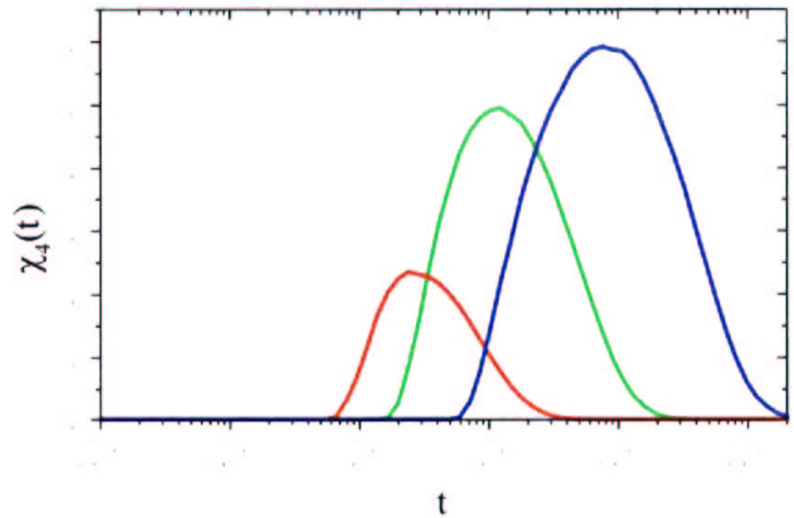
Beyond 1-loop

$$\chi_4(t) \sim \int_0^t d\tau \sum_k \sum_q Q^{(1)}_{k,q} F(|k-q|, t-\tau) F(q, t-\tau) \frac{dF(k,\tau)}{d\tau}$$

$$+ \int_0^t d\tau \sum_k \sum_q Q^{(2)}_{k,q} F(|k-q|, \tau) F(q, \tau) \frac{dF(q, t-\tau)}{d\tau}$$

$$+ \cdots$$

Depend on liquid structure



Demonstrates precise connection between peak of $\chi_4(t)$ and α-relaxation time.

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