



# Mode Coupling Theory for Normal and Supercooled Quantum Liquids

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# Open Problems: Why and How?

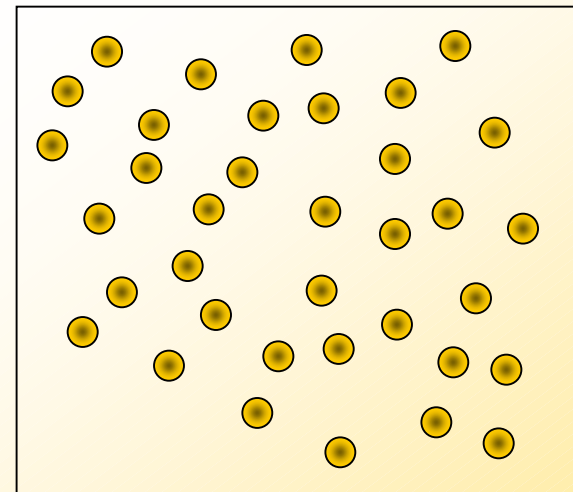


- Perturbation theory
  - FGR
  - Pade
- Reduced dynamics
  - Markov
  - Memory effects
- Harmonic bath approximation
  - Path integration
  - Influence functional
- Mean Field treatments
  - TDH/TDDFT
  - MC-TDH
- Semiclassical methods
  - MQC
  - CMD
  - SC-IVR/FB
  - Gaussian
- Analytic continuation
  - Imaginary time path integrals
  - MaxEnt/Svd



# What Problems

- Neat Liquids
  - Superfluid helium
  - Less quantum solvents, like hydrogen.
- System-Bath Dynamics
  - Reaction dynamics.
  - Spectroscopy.
  - Nonadiabatic dynamics.
- Quantum glasses





# Outline – First Part

- Generalized Langevin Equation
  - Nakajima-Zwanzig-Mori projection operator technique.
  - Derivation of an exact GLE.
  - No harmonic approximation
- Classical Mode-Coupling Theory
  - Useful approximations to the memory kernel.
  - Short and long time.
  - Götze and Lücke, Sjögren and Sjölander approximation to the long time memory kernel.
- Some Application to Classical Systems.
  - Density fluctuations in liquid lithium.
  - The glass transition.

# Outline – Second Part



- Quantum Mode-Coupling Theory
  - Quantum generalized Langevin equation (QGLE).
  - A natural formulation – Kubo.
  - Quantum mode-coupling approximations.
  - Analysis of the theory.
- Quantum Mass Transport
- Quantum Density Fluctuations
  - Application to Normal Liquids.
  - Application to supercooled binary mixtures.



# Literature

- E. Rabani and D.R. Reichman, J. Phys. Chem. B 105, 6550 (2001).
- D.R. Reichman and E. Rabani, Phys. Rev. Lett. 87, 265702 (2001).
- E. Rabani and D.R. Reichman, Phys. Rev. E. 65, 036111 (2002).
- E. Rabani and D.R. Reichman, J. Chem. Phys. 116, 6271 (2002).
- D.R. Reichman and E. Rabani, J. Chem. Phys. 116, 6279 (2002).
- E. Rabani, D.R. Reichman, G. Krilov, and B.J. Berne, PNAS USA 99, 1129 (2002).
- E. Rabani and D.R. Reichman, Europhys. Lett. 60, 656 (2002).
- E. Rabani, in Proceedings of "The Monte Carlo Method in the Physical Sciences: Celebrating the 50th anniversary of the Metropolis algorithm", AIP Conference Proceedings, vol. 690, 281 (2003).
- E. Rabani and D.R. Reichman, J. Chem. Phys. 120, 1458 (2004).
- E. Rabani and D.R. Reichman, Ann. Rev. Phys. Chem., in press.
- E. Rabani, K. Miyazaki, and D.R. Reichman, submitted.

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# First Part



# Generalized Langevin Equation



Consider a classical system of  $n$  particles with Hamiltonian  $H$ . Lets focus on  $m < n$  dynamical variables ( $A_1 \dots A_m$ ). These variable obey the classical equations of motion given by:

$$\frac{dA_i(t)}{dt} = \{A_i(t), H\} \equiv iLA_i(t)$$

The Liouvillian is defined as (we assume that particles interact through a pair potential)

$$iL = \sum_i \frac{p_i}{m_i} \frac{\partial}{\partial r_i} - \sum_{i>j} \frac{\partial \phi(r_{ij})}{\partial r_i} \frac{\partial}{\partial p_i}$$

Formal (but not useful) solution:

$$A_i(t) = \exp(iLt) A_i(0)$$

The above equation can be written in a **different way**, which can be used as a starting point for approximate methods.



# Scalar Products and Projections



Lets first define the **scalar product** of two dynamical variables:

$$(A, B) = \langle A^* B \rangle$$

If we focus on the  $m$  components of  $A$ , we can think of these components as forming a set of “**directions**” in the complex vector space composed of all dynamical functions. For example, if  $(A_i, A_j) = \delta_{ij}$  then the set is an orthonormal set spanning the  $m$  dimensional subspace of all dynamical variables. The  $A_i$ 's can be viewed as unit vectors.

Lets define a **projection** onto this space:

$$P = (A, \dots) \cdot (A, A)^{-1} \cdot A$$

$$PA = A$$

$$P^2 = P$$



# Classical GLE

Lets look again at the evolution of  $A$ :

$$A_i(t) = \exp(iLt) A_i(0)$$

and take the time derivative of both sides ( $P = (A, \dots) \cdot (A, A)^{-1} \cdot A$ ):

$$\begin{aligned} \frac{dA(t)}{dt} &= \exp(iLt) iLA(0) = \exp(iLt) [P + (1-P)] \dot{A}(0) \\ &\equiv i\Omega \cdot A(t) + \exp(iLt) Q\dot{A}(0) \end{aligned}$$

here  $Q = 1 - P$  and  $i\Omega = (A, \dot{A}) \cdot (A, A)^{-1}$

Now, we decompose  $\exp(iLt)$  and solve for  $g(t)$ :

$$\exp(iLt) \equiv \exp(iQLt) + g(t)$$

$$iL \{ \exp(iQLt) + g(t) \} = iQL \exp(iQLt) + \dot{g}(t)$$

$$\dot{g}(t) = iLg(t) + iPL \exp(iQLt)$$

$$g(t) = \int_0^t d\tau \exp(iL(t-\tau)) iPL \exp(iQL\tau)$$

Full propagator:  $\exp(iLt)$

Projected propagator:  $\exp(iQLt)$



# Classical GLE cont.

Now, we take the solution for  $g(t)$  and plug it into the full propagator:

$$\exp(iLt) \equiv \exp(iQLt) + \int_0^t d\tau \exp(iL(t-\tau)) iPL \exp(iQL\tau)$$

We would like to use this in the equation for  $A_i(t)$ :

$$\frac{dA(t)}{dt} = i\Omega \cdot A(t) + \exp(iLt) Q\dot{A}(0)$$

Lets define  $f(t)$  - the **fluctuating** (random) **force**:

$$f(t) = \exp(iQLt) iQLA(0)$$

Note that random force is orthogonal to  $A$  at all times

( $PA = A \rightarrow QA = (1-P)A = 0$ ):

$$\begin{aligned} (A, f(t)) &= (A, \exp(iQLt) iQLA(0)) = (A, iQL \exp(iQLt) A(0)) = \\ &= (QA, iL \exp(iQLt) A(0)) = 0 \end{aligned}$$

This is important for future use.



# Classical GLE cont.

Using the following relations:

$$i(PLA, f(t)) = i(A, LA)(A, A)^{-1}(A, f(t)) = 0$$

$$i(A, Lf(t)) = i(LA, f(t)) = i((1-P)LA, f(t)) = -(f(0), f(t))$$

we arrive at

$$\begin{aligned} \exp(iLt)QA\dot{A}(0) &= \left\{ \exp(iQLt) + \int_0^t d\tau \exp(iL(t-\tau))iPL \exp(iQL\tau) \right\} iQLA(0) \\ &= \int_0^t d\tau \exp(iL(t-\tau))iPLf(\tau) + f(t) \\ &= -\int_0^t d\tau (f(0), f(\tau))(A, A)^{-1} A(t-\tau) + f(t) \end{aligned}$$

Now we are ready to obtain our final equation starting from the following exact expression:

$$\frac{dA(t)}{dt} = i\Omega \cdot A(t) + \exp(iLt)QA\dot{A}(0)$$

# Generalized Langevin Equation



Using these relations we arrive at the **exact** generalized Langevin equation give by

$$\frac{dA(t)}{dt} = i\Omega \cdot A(t) - \int_0^t d\tau K(\tau) A(t-\tau) + f(t) \quad \left( \frac{dA(t)}{dt} = \{A(t), H\} \equiv iLA(t) \right)$$

where the **memory kernel**  $K(t)$  is given by (fluctuation-dissipation)

$$K(t) = (f(0), f(t)) \cdot (A, A)^{-1}$$

and the **fluctuating random force** is given by

$$f(t) = \exp(iQLt) iQLA(0)$$

We can also express the above GLE as an equation for the **correlation function** ( $C(t) = (A(0), A(t)) = \langle A^*(0)A(t) \rangle$ )

$$\frac{dC(t)}{dt} = i\Omega \cdot C(t) - \int_0^t d\tau K(\tau) C(t-\tau)$$



# Discussion of the GLE

- So far, what we have done is just to **rephrase** the the classical equation of motion for  $A(t)$ . In fact, since  $f(t)$  involves the projected propagator ( $\exp(iQLt)$ ), it is **more difficult** to calculate  $f(t)$ , than to solve for  $A(t)$  directly!
- However, if we can come up with a useful approximation for  $K(t)$ , then we may find that this **rephrasing** of the equations for  $A(t)$  is indeed **useful**.
- Lets consider a simple example where  $A(t)$  is the **velocity of a tagged liquid particle** in a monoatomic liquid. The exact GLE for the velocity autocorrelation function is ( $C_v(t) = \langle v(0)v(t) \rangle$ ):

$$\frac{dC_v(t)}{dt} = -\int_0^t d\tau K_v(\tau)C_v(t-\tau)$$





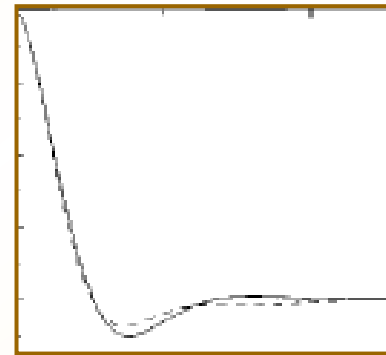
# Simple example

Now, let's make a **simple Gaussian** approximation to the memory kernel:

$$K_v(t) = K_v(0) \exp\left(-\frac{t^2}{\tau^2}\right)$$

$$K_v(0) = \beta m \langle \dot{v}^2 \rangle \equiv \Omega_0^2$$

$$\tau = \sqrt{\frac{2\Omega_0^2}{\Omega_0^4 - \beta m \langle \dot{v}^2 \rangle}}$$



Even this simple approximation (short time expansion) **captures** some of the hallmarks of normal monoatomic liquids. The reason is that the approximation is done at the level of the memory kernel, and thus better results are obtained for the correlation function itself.

However, this approximation completely neglects the long time decay of the memory kernel.



# Classical Mode-Coupling Theory

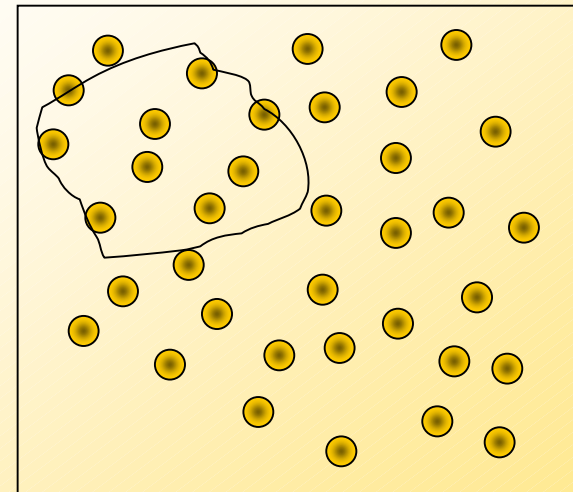


To properly describe the long time decay of the memory kernel, it is useful to look at dynamical variables that are **slowly evolving**, nearly conserved. What does this mean?

In a liquid, some quantities, like the total number of particles, the total energy, the total angular momentum, the total momentum, etc. are strictly conserved:

$$\frac{dN}{dt} = \frac{dE}{dt} = \frac{dL}{dt} = \frac{dP}{dt} = 0$$

Now, consider the total number of particles in a large volume, but not the entire system. As the size of the volume approaches the entire box,  $N(t)$  becomes time independent. But for large regions, **the timescale of fluctuations of  $N$  will be very slow.**





# Slow Variables

Mathematically, it is useful to define **wave vector** dependent quantities:

$$n_k(t) = \sum_{i=1}^N \exp(ikr_i(t)) = \int d^3r \exp(ikr) \sum_{i=1}^N \delta(r - r_i(t))$$

$$j_k(t) = \sum_{i=1}^N v_i \exp(ikr_i(t)) = \int d^3r \exp(ikr) \sum_{i=1}^N v_i \delta(r - r_i(t))$$

The former is simply the Fourier transform of the **total density**, and the latter is the Fourier transform of the **total momentum density**.

As  $k \rightarrow 0$  these quantities become conserved, and therefore at low values of  $k$  they will **vary slowly!**

$$F(k, t) = \frac{1}{N} \langle n_k^*(0) n_k(t) \rangle \quad \text{Intermediate scattering function}$$

$$J(k, t) = \frac{1}{N} \langle j_k^*(0) j_k(t) \rangle \quad \text{Current correlation function}$$

# Other Useful Slow Variables



Other slow variables are

$$c_k(t) = \exp(ikr_i(t)) = \int d^3r \exp(ikr) \delta(r - r_i(t))$$

$$j_k^i(t) = v_i \exp(ikr_i(t)) = \int d^3r \exp(ikr) v_i \delta(r - r_i(t))$$

The former is simply the Fourier transform of the **single particle density**, and the latter is the Fourier transform of the **single particles momentum density**. The corresponding correlation functions are

$$F_s(k, t) = \frac{1}{N} \langle c_k^*(0) c_k(t) \rangle$$

Self intermediate scattering function

$$J_i(k, t) = \frac{1}{N} \langle j_k^{i*}(0) j_k^i(t) \rangle$$

Self current correlation function



# A Small Paradox

The point is that if we believe that the set of dynamical variables  $\{A_i\}$  contains all the **important** slow variables, then our projection operator  $P$  projects onto the subspace that evolves slowly. And  $Q=1-P$  projects onto the fast subspace. Accordingly, we can interpret the random force  $f(t) = \exp(iQLt)Q\dot{A}(0)$  as: Take the fast part of  $\dot{A}(0)$  and evolve it in the fast part of phase space.

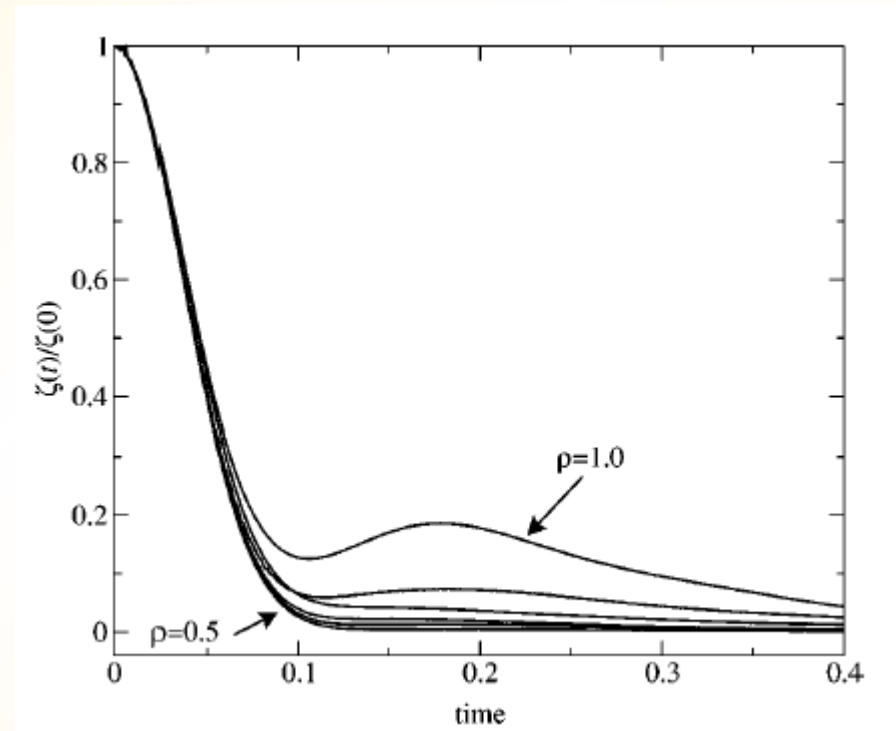
Thus, we expect the memory kernel  $K(t)$  (which is proportional to the autocorrelation of the random force) to decay very rapidly, and perhaps approximate it by  $K(t) = K(0)\delta(t)$ .

**This is not the case!**



# A Typical Memory Kernel

A typical memory kernel for the velocity autocorrelation function of a Lennard-Jones fluid at different solvent densities. Not the **fast** component, followed by a **slower** component. The slow component becomes more dominant at higher liquid densities.



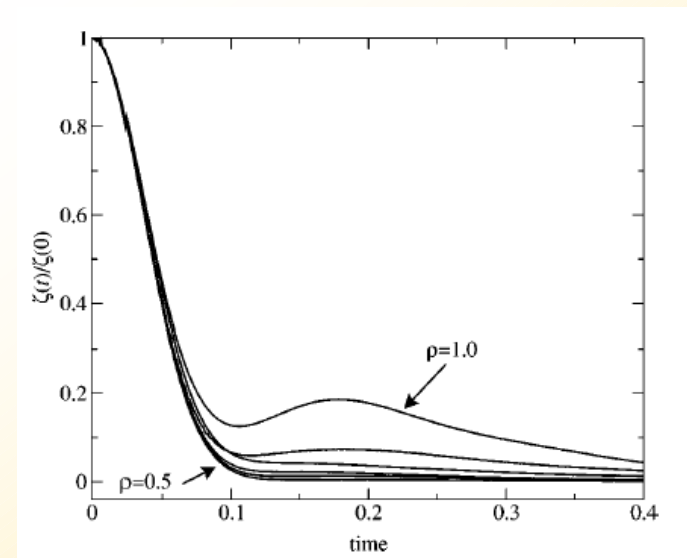


# Where Does the Slow Part Come From?

Our simple picture assumes that the set  $\{A_i\}$  includes all slow modes is not quite correct. If  $A_i$  is slow, so is  $A_i A_j$ , etc. In other words, the **products of slow variables** are also **slow**!

Thus, we expect that at short times  $K(t)$  will indeed decay quickly, but at longer times it will have a slow component, which will be dominated by the slow modes that have not been included in the set  $\{A_i\}$ .

We can then “**engineer**” a memory function with the above qualities, with some additional approximations. Lets look at an example.







# Mode Coupling Approximation

Lets focus on again on the **velocity autocorrelation function**. The exact GLE is given by ( $C_v(t) = \langle v_i(0)v_i(t) \rangle$ ):

$$\frac{dC_v(t)}{dt} = -\int_0^t d\tau K_v(\tau)C_v(t-\tau)$$

The **frequency** in this case equals zero:

$$i\Omega = (A, \dot{A}) \cdot (A, A)^{-1} = \langle v_i \dot{v}_i \rangle \cdot \langle v_i v_i \rangle^{-1} = \langle v_i \rangle \left\langle -\sum_j \frac{\partial \phi(r_{ij})}{\partial r_i} \right\rangle \left( \frac{KT}{M} \right)^{-1} = 0$$

The **memory kernel**  $K(t)$  is given by the exact equation:

$$K(t) = (f(0), f(t)) \cdot (v_i, v_i)^{-1} = \left( \frac{k_B T}{m} \right)^{-1} (f(0), f(t))$$

and the **fluctuating random force** is given by

$$f(t) = \exp(iQLt) iQLA = \exp(iQLt) (1-P) \dot{v}_i = \exp(iQLt) \dot{v}_i$$

since

$$(1-P) \dot{v}_i = \dot{v}_i - (v_i, \dot{v}_i) \cdot (v_i, v_i) v_i = \dot{v}_i$$





# Classical MCT cont.

Putting all together, we arrive at a simple expression for the memory kernel, which is exact, and involves the projected propagation of the force on particle  $i$ :

$$K_v(t) = \left( \frac{k_B T}{m} \right)^{-1} \langle \dot{v}_i \exp(iQLt) \dot{v}_i \rangle$$

At **short times**, the decay of the memory kernel is expected to be rapid, and we can use the short time expansion discussed before:

$$K_v^{FAST}(t) = K_v(0) \exp\left(-\frac{t^2}{\tau^2}\right)$$

$$K_v(0) = \beta m \langle \dot{v}^2 \rangle \equiv \Omega_0^2$$

$$\tau = \sqrt{\frac{2\Omega_0^2}{\Omega_0^4 - \beta m \langle \ddot{v}^2 \rangle}}$$

Note that this gives a microscopic meaning in terms of well defined **structural properties** of a liquid.



# Classical MCT cont.

Now, we can rewrite the total memory kernel as follows:

$$K_v(t) = K_v^{FAST}(t) + (K_v(t) - K_v^{FAST}(t)) \approx K_v^{FAST}(t) + K_v^{MCT}(t)$$

Lets keep in mind that  $K_v^{MCT}(t)$  **varies slowly**. Thus at longer time, we expect the fast part to diminish, and the slow part will be dominated by those modes in the liquid that decay slowly. Hence, we make the following (**ad-doc**) approximation:

$$K_v^{MCT}(t) = \left( \frac{k_B T}{m} \right)^{-1} \langle \dot{v}_i P_m \exp(iLt) P_m \dot{v}_i \rangle$$

And the new projector  $P_m$  operator projects  $\dot{v}_i$  onto the slow modes. As a first approximation, we can take the slow modes to be a combination of **single and collective densities**, with conservation of momentum:

$$P_m = \sum_k \frac{\langle A_k^*, \dots \rangle}{\langle A_k^* A_k \rangle} A_k = \sum_k \frac{\langle A_k^*, \dots \rangle}{NS(k)} A_k$$

$$A_k = c_k^* n_k = c_{-k} n_k$$

$$n_k = \sum_{i=1}^N \exp(ikr_i)$$

$$c_k = \exp(ikr_i)$$



# Classical MCT cont.

Now, let's plug this back into the expression for the MCT memory kernel. After some tedious algebra we obtain:

$$K_v^{MCT}(t) = \left( \frac{k_B T m n^2}{N^2} \right) \sum_{k, k'} (k \cdot k') c(k) c(k') \langle A_k^*(0) A_k(t) \rangle$$

$$c(k) = \frac{1}{n} \left( 1 - \frac{1}{S(k)} \right)$$

We make a **factorization** approximation (in fact we made one already for the projection onto the slow modes):

$$\begin{aligned} \langle A_k^*(0) A_{k'}(t) \rangle &= \langle c_k(0) n_{-k}(0) c_{-k'}(t) n_{k'}(t) \rangle \approx \\ &\langle c_k(0) c_{-k'}(t) \rangle \langle n_{-k}(0) n_{k'}(t) \rangle = N F_s(k, t) F(k, t) \delta_{kk'} \end{aligned}$$

Plugging this into the above expression, making use of the delta function, and replacing the **sum** of  $k$  with an **integral**, we arrive at:

$$K_v^{MCT}(t) = \left( \frac{m k_B T n}{2\pi^2} \right) \int_0^\infty dk k^4 c^2(k) F_s(k, t) F(k, t)$$



# Classical MCT (final)

We need to combine the **fast** and **slow** parts. However, our expression for the fast term is exact to second order in time. We thus need to subtract the inertial part from the slow kernel. Otherwise, we will over count the memory kernel at short times.

$$K_v(t) \approx K_v^{FAST}(t) + K_v^{MCT}(t) = \\ K_v(0) \exp\left(-\frac{t}{\tau}\right) + \left(\frac{mk_B T n}{2\pi^2}\right) \int_0^\infty dk k^4 c^2(k) \left(F_s(k,t) - F_s^0(k,t)\right) F(k,t)$$

where  $F_s^0(k,t)$  is the “free particle” self intermediate scattering function given by:

$$F_s^0(k,t) = \exp\left(-\frac{k_B T}{2m} k^2 t^2\right)$$

## What have we done?



# Summary of MCT

We start from an **exact** GLE:

$$\frac{dC_v(t)}{dt} = -\int_0^t d\tau K_v(\tau) C_v(t-\tau) \quad K_v(t) = \left(\frac{k_B T}{m}\right)^{-1} \langle \dot{v}_i \exp(iQLt) \dot{v}_i \rangle$$

Decompose the memory kernel to a **fast** and **slow** portions:

$$K_v(t) \approx K_v^{FAST}(t) + K_v^{MCT}(t)$$

$$K_v^{FAST}(t) = K_v(0) \exp\left(-(t/\tau)^2\right)$$

$$K_v^{MCT}(t) = \left(\frac{mk_B T n}{2\pi^2}\right) \int_0^\infty dk k^4 c^2(k) \left(F_s(k,t) - F_s^0(k,t)\right) F(k,t)$$

And continue until we have a closure, namely, that our equations describe all **necessary** correlation functions.

## Why Mode Coupling?

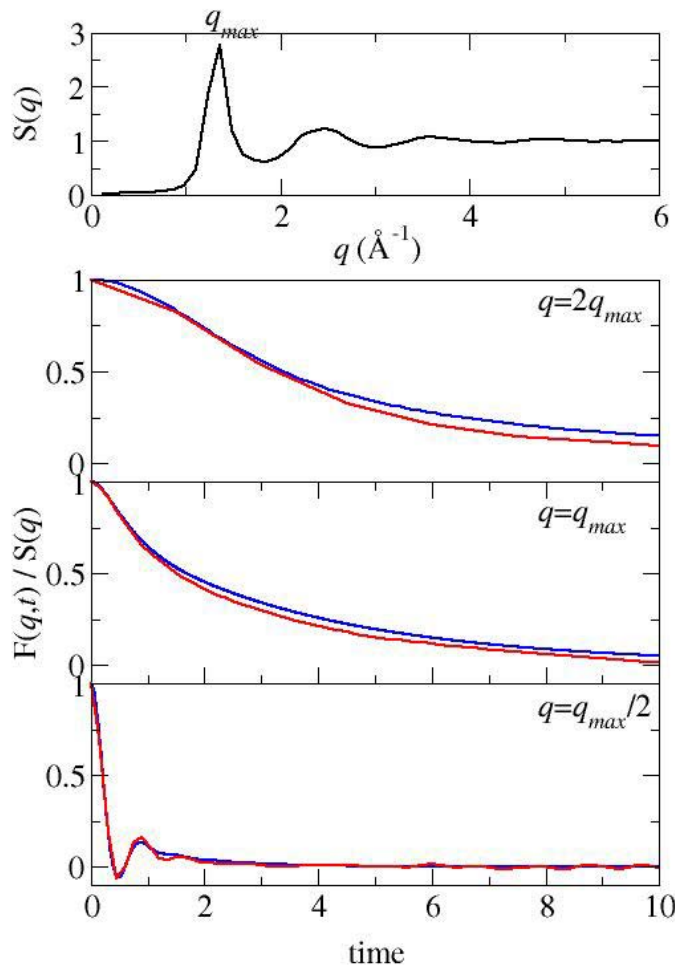


# Some Interesting Applications





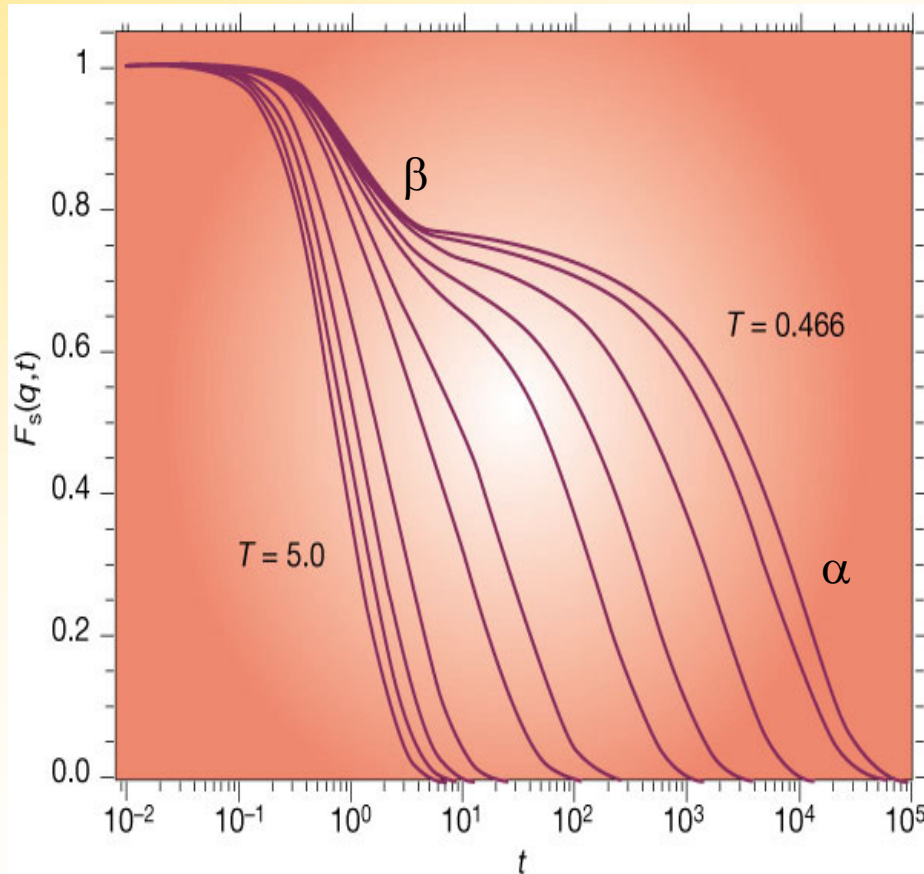
# Mode-Coupling Theory for Classical Liquids



The normalized intermediate scattering function for liquid *lithium*. The red curves are results obtained from molecular dynamics simulations and the blue curves are results obtained from a classical mode-coupling theory. The agreement between the theory and simulations is remarkable for all  $q$  values shown.



# Prediction for Classical Glasses



## MCT predictions

Early  $\beta$

$$F_s(k, t) = f + A_1 t^{-a}$$

Late  $\beta$

$$F_s(k, t) = f - A_2 t^b$$

$\alpha$  regime

$$F_s(k, t) = \exp\left\{-\left(\frac{t}{\tau}\right)^\beta\right\}$$



# Second Part



# Outline – Second Part

- Quantum Mode-Coupling Theory
  - Quantum generalized Langevin equation (QGLE).
  - A natural formulation – Kubo.
  - Quantum mode-coupling approximations.
  - Analysis of the theory.
- Quantum Mass Transport
- Quantum Density Fluctuations
  - Application to Normal Liquids.
  - Application to supercooled binary mixtures.



# Quantum Transport

# Outline of Quantum Approach



- **Step 1:** Formulation of an exact quantum generalized Langevin equation (**QGLE**) using Zwanzig-Mori projection operator technique, for the **Kubo transform** of the dynamical variable of interest.
- **Step 2:** Approximate memory kernel for the QGLE using a **quantum mode-coupling** theory.
- **Step 3:** Solution of the QGLE with the approximate memory kernel combined with exact static input generated from a suitable **PIMC** scheme.



# QGLE for VACF

We need to obtain a QGLE for the **velocity autocorrelation function** ( $v$  is the velocity of a tagged liquid particle along an arbitrary direction):

$$C_v^K(t) = \langle \hat{v}_i, \hat{v}_i^K(t) \rangle \quad \hat{v}_i^K(t) = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\lambda e^{-\lambda\hat{H}} e^{i\hat{H}t} v_i e^{-i\hat{H}t} e^{\lambda\hat{H}}$$

Following similar lines to those sketched for the classical theory, we obtain an **exact quantum generalized Langevin equation** (QGLE):

$$\frac{dC_v^K(t)}{dt} + \int_0^t d\tau K_v^K(t-\tau) C_v^K(\tau) = 0$$

where we have used the following projection operator

$$P_v^K = \frac{\langle \hat{v}_i, \dots \rangle}{\langle \hat{v}_i, \hat{v}_i^K \rangle} \hat{v}_i^K$$

and the memory kernel is **formally** given by

$$K_v^K(t) = \frac{1}{\langle \hat{v}_i, \hat{v}_i^K \rangle} \left\langle \dot{\hat{v}}_i, e^{i(1-P_v^K)\hat{L}t} \dot{\hat{v}}_i^K \right\rangle$$

# Quantum Mode Coupling Theory



The Kernel is approximated by

$$K_v^\kappa(t) = K_{v,b}^\kappa(t) + K_{v,m}^\kappa(t)$$

Fast decaying quantum **binary** term:

$$K_{v,b}^\kappa(t) = K_v^\kappa(0) f(t/\tau)$$

$$\tau = - \left( \frac{\langle \ddot{\hat{v}}, \ddot{\hat{v}}^\kappa \rangle}{\langle \dot{\hat{v}}, \dot{\hat{v}}^\kappa \rangle} + \frac{\langle \dot{\hat{v}}, \dot{\hat{v}}^\kappa \rangle}{\langle \hat{v}, \hat{v}^\kappa \rangle} \right)^{-1/2}$$

The slow decaying **quantum mode-coupling** term:

$$K_{v,m}^\kappa(t) \approx \frac{1}{2\pi^2 n \langle \hat{v}, \hat{v}^\kappa \rangle} \int_0^\infty dq q^2 |V_v^\kappa(q)|^2 \left( F_s^\kappa(q,t) - F_{s,b}^\kappa(q,t) \right) F^\kappa(q,t)$$

The vertex:

$$V_v^\kappa(q) = \frac{\langle \hat{b}_q^*, \dot{\hat{v}}^\kappa \rangle}{N F_s^\kappa(q,0) S^\kappa(q)}$$

$$\hat{b}_q = \sum_{\alpha \neq 1} e^{iq(\hat{r}_\alpha - \hat{r}_1)} = \hat{c}_q \hat{n}_{-q}$$





# MC Memory Kernel for VACF

The slow decaying quantum mode-coupling term is obtained using a set of approximations. The **projected dynamics** is replaced with the **full dynamics** projected onto the slow decaying modes:

$$e^{i(1-P_v^\kappa)\hat{L}t} \Rightarrow P_m^\kappa e^{i\hat{L}t} P_m^\kappa$$

where the **new projection** operator is given by:

$$P_m^\kappa = \sum_q \frac{\hat{b}_q^\kappa \langle \hat{b}_q^*, \dots \rangle}{NF_s^\kappa(q, 0) S^\kappa(q)}$$

In addition, **four point** correlation functions are replaced by a product of **two point** correlation functions:

$$\langle \hat{b}_{-q}, \hat{b}_q^\kappa(t) \rangle \approx \langle \hat{c}_{-q}, \hat{c}_q^\kappa(t) \rangle \langle \hat{n}_{-q}, \hat{n}_q^\kappa(t) \rangle = F_s^\kappa(q, t) F^\kappa(q, t)$$



# PIMC Scheme

We need to calculate the following static Kubo transforms:

$$\langle \hat{O}, \hat{O}^\kappa \rangle = \frac{1}{\beta \hbar Q} \int_0^{\beta \hbar} d\lambda \text{Tr} \hat{O} e^{-\lambda H} \hat{O} e^{-(\beta - \lambda) H} \quad \text{where} \quad \hat{O} = G(\hat{r}) \hat{p} + \hat{p} G(\hat{r})$$

Using the coordinate representation of the matrix element:

$$\langle r' | G(\hat{r}) \hat{p} + \hat{p} G(\hat{r}) | r \rangle = i \hbar (G(r) \nabla_{r'} \delta(r - r') - G(r') \nabla_r \delta(r - r'))$$

We obtain (to lowest order in  $\varepsilon$  using  $P$  Trotter slices):

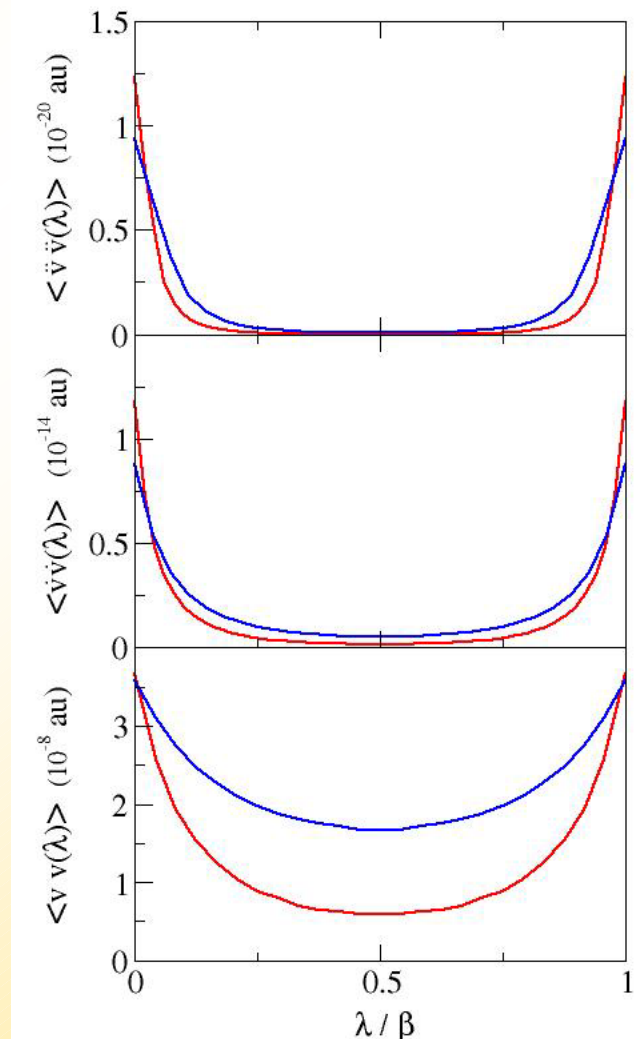
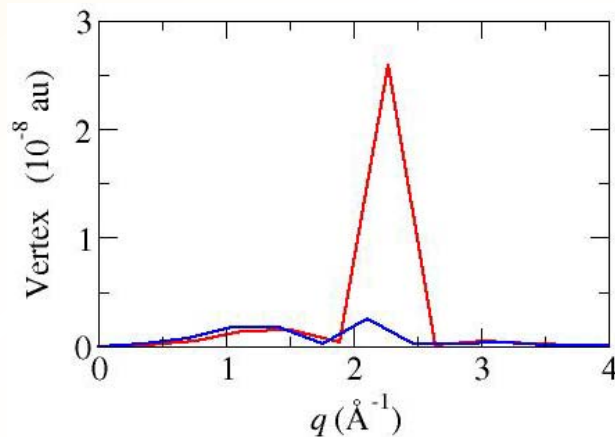
$$\begin{aligned} \langle \hat{O}, \hat{O}^\kappa \rangle = & -\frac{m^2}{\varepsilon \beta \hbar} \sum_{j=1}^P \int dr_1 \cdots dr_P P(r_1 \cdots r_P) G(r_1) G(r_{P-j+1}) \\ & \times (r_2 - r_P) \cdot (r_{P-j+2} - r_{P-j}) \end{aligned}$$

Our result looks similar to the Barker energy estimator, however, it is numerically less noisy.

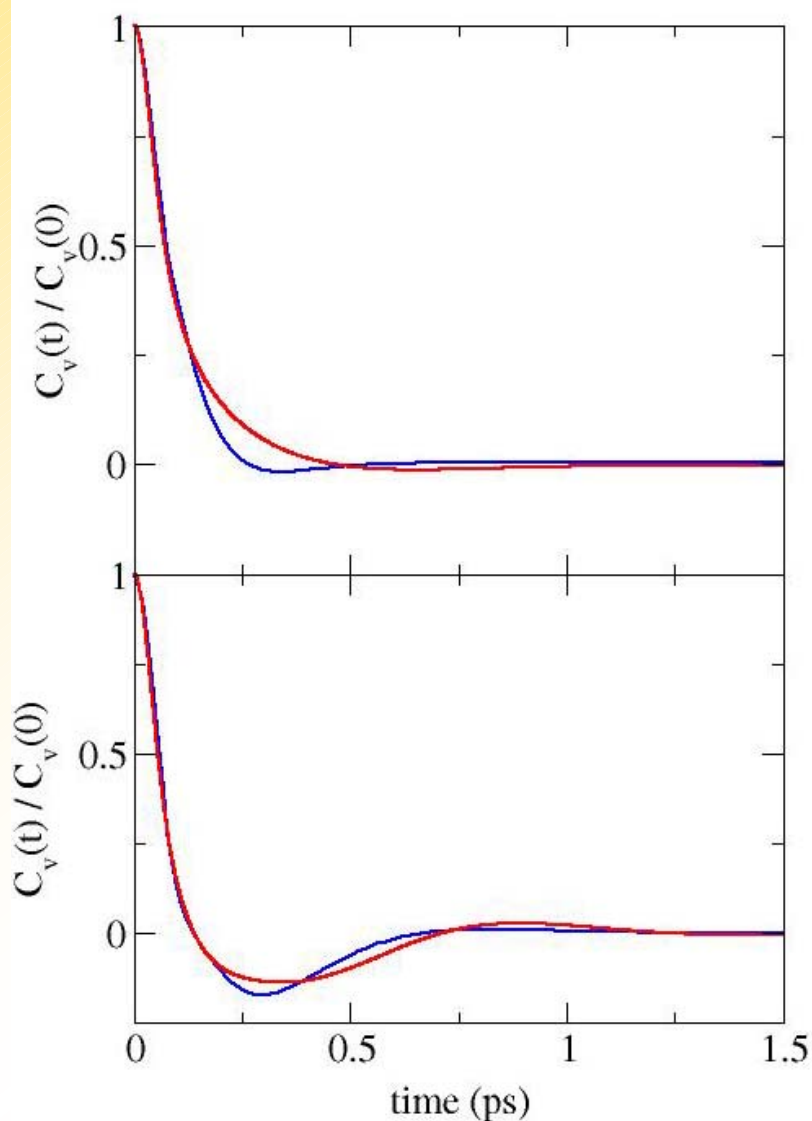
# Static input from PIMC



The static input for the memory kernel of the velocity autocorrelation function generated from a PIMC simulation method for liquid *para*-hydrogen at  $T=14\text{K}$  (red curve) and  $T=25\text{K}$  (blue curve).



# Velocity autocorrelation function

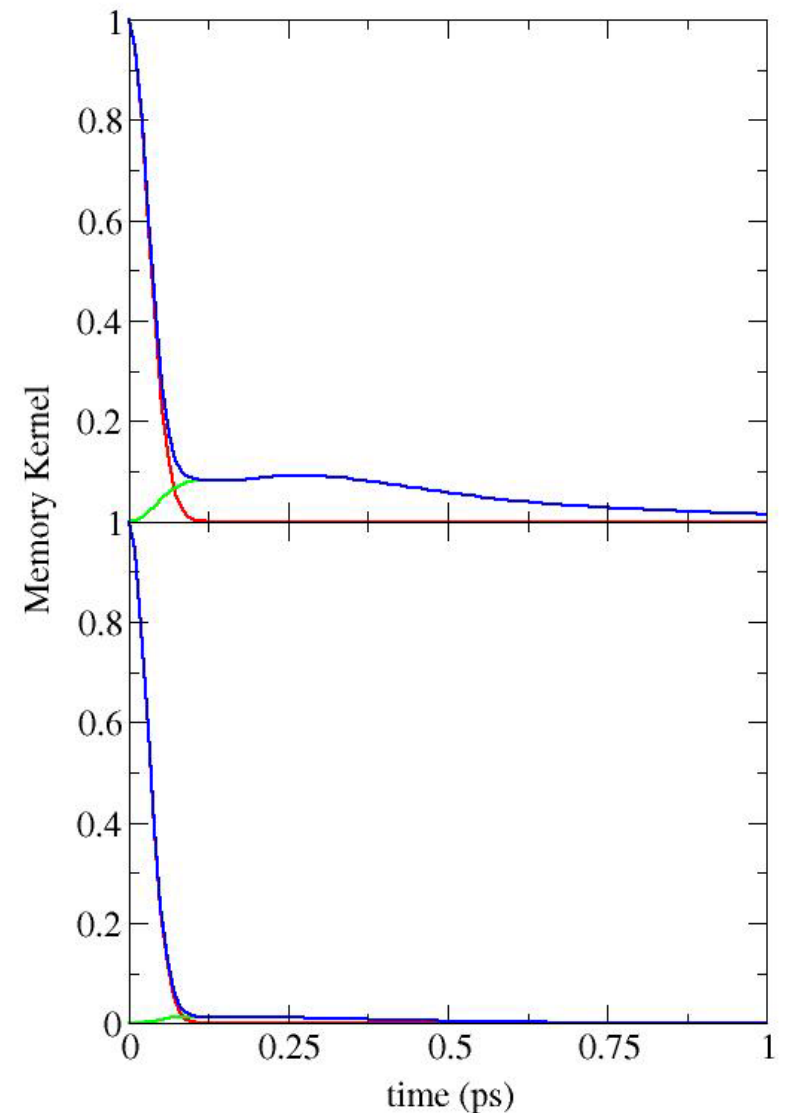


The normalized velocity autocorrelation function calculated from the quantum mode-coupling theory (red curve) and from an analytic continuation of imaginary-time PIMC data (blue curve) for liquid *para*-hydrogen at T=14K (lower panel) and T=25K (upper panel). The good agreement between the two methods is a strong support for the accuracy of the quantum mode-coupling approach for liquid *para*-hydrogen.



# Memory kernel for VACF

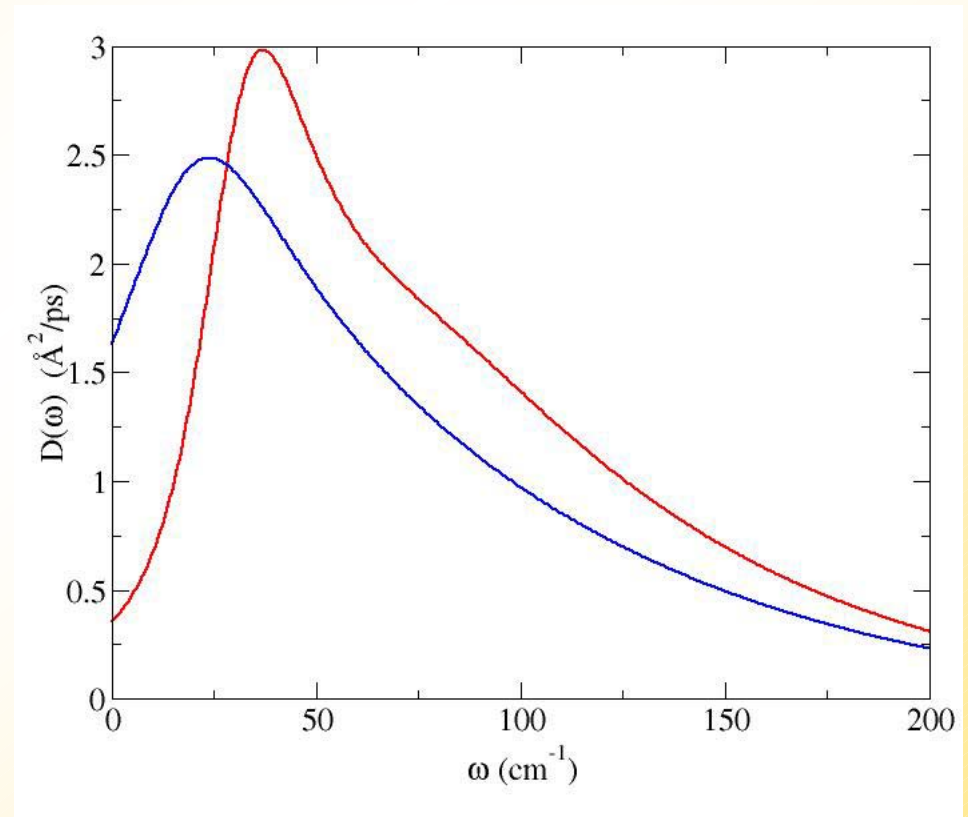
The Kubo transform of the memory kernel for the velocity autocorrelation function for liquid para-hydrogen at  $T=14\text{K}$  (upper panel) and  $T=25\text{K}$  (lower panel). Shown are the fast-decaying binary term (red curve), the slow-decaying mode-coupling term (green curve) and the total memory kernel (blue curve). The contribution of the slow mode-coupling portion of the memory kernel is significant at the low temperature, while at the high temperature, the kernel can be approximated by only the fast binary portion.





# Self-diffusion - liquid *para*-hydrogen

The frequency dependent diffusion constant for liquid *para*-hydrogen at T=14K (red curve) and T=25K (blue curve). The self-diffusion obtained from the Green-Kubo relation is 0.30 and 1.69 ( $\text{\AA}^2/\text{ps}$ ) for T=14K and T=25K, respectively. These results are in good agreement with the experimental results (0.40 and 1.60) and with the maximum entropy analytic continuation method (0.28 and 1.47, Rabani *et al.*, PNAS 99, 1129-1133 (2002)).







# Density Fluctuations

# QGLE for Density Fluctuations



To study density fluctuations we need to specify the dynamical variable and the corresponding correlation function (the intermediate scattering function):

$$\hat{n}_q = \sum_{j=1}^N \exp(iq \cdot \hat{r}_j)$$

$$F^\kappa(q, t) = \frac{1}{N} \langle \hat{n}_q^*, \hat{n}_q^\kappa(t) \rangle$$

$$\hat{j}_q = \frac{1}{2m} \sum_{i=1}^N \hat{p}_i \exp(iq \cdot \hat{r}_i) + \exp(iq \cdot \hat{r})_i \hat{p}_i$$

$$J^\kappa(q, t) = \frac{1}{N} \langle \hat{j}_q^*, \hat{j}_q^\kappa(t) \rangle$$

The **exact** QGLE for the Kubo transform of the intermediate scattering function is given by

$$\frac{d^2 F^\kappa(q, t)}{dt^2} + \omega_\kappa^2(q) F^\kappa(q, t) + \int_0^t dt' K^\kappa(q, t-t') \frac{dF^\kappa(q, t')}{dt'} = 0$$

The formal expression for the memory kernel is

$$K^\kappa(q, t) = \frac{1}{N J_q^\kappa} \left\langle \hat{R}_q^*, \exp(i(1 - P_q^\kappa) \hat{L} t) \hat{R}_q^\kappa \right\rangle$$

$$\hat{R}_q = \dot{\hat{j}}_q - iq \frac{J^\kappa(q)}{S^\kappa(q)} \hat{n}_q$$

# Mode Coupling Approximation



Mode-coupling approximations for the memory kernel

$$K^\kappa(q, t) = K_b^\kappa(q, t) + K_{mct}^\kappa(q, t)$$

The projected dynamics is replaced with the full dynamics projected onto the slow decaying modes:

$$e^{i(1-P_q^\kappa)\hat{L}t} \Rightarrow P_{mq}^\kappa e^{i\hat{L}t} P_{mq}^\kappa$$

where the new projection operator  $P_{mq}^\kappa$  projects onto the following slow modes:

$$\hat{b}_{k, q-k} = \hat{n}_k \hat{n}_{q-k}$$

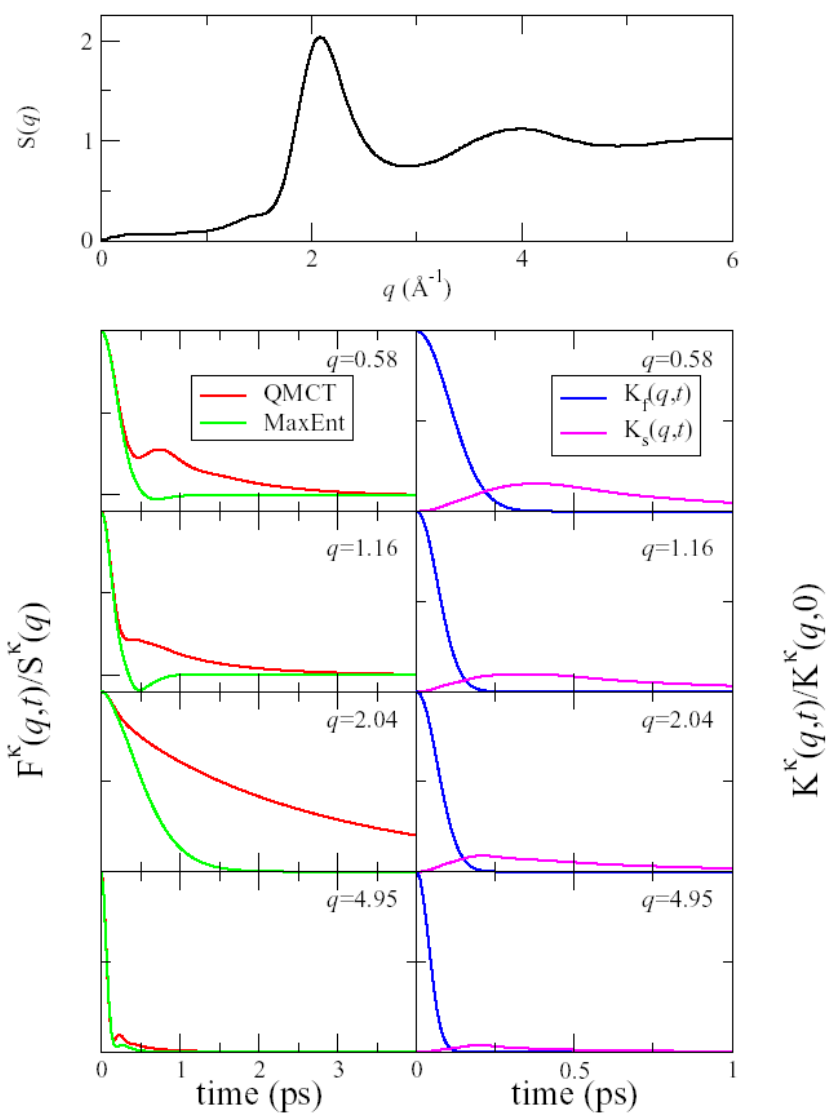
In addition, four point correlation functions are replaced by a product of two point correlation functions.

$$\langle \hat{b}_{k, q-k}^*, \hat{b}_{k, q-k}(t) \rangle \approx \langle \hat{n}_k^*, \hat{n}_k(t) \rangle \langle \hat{n}_{q-k}^*, \hat{n}_{q-k}(t) \rangle = F^\kappa(k, t) F^\kappa(q-k, t)$$



# Application to Normal Quantum Liquids

# Quantum Liquids $o\text{-D}_2$

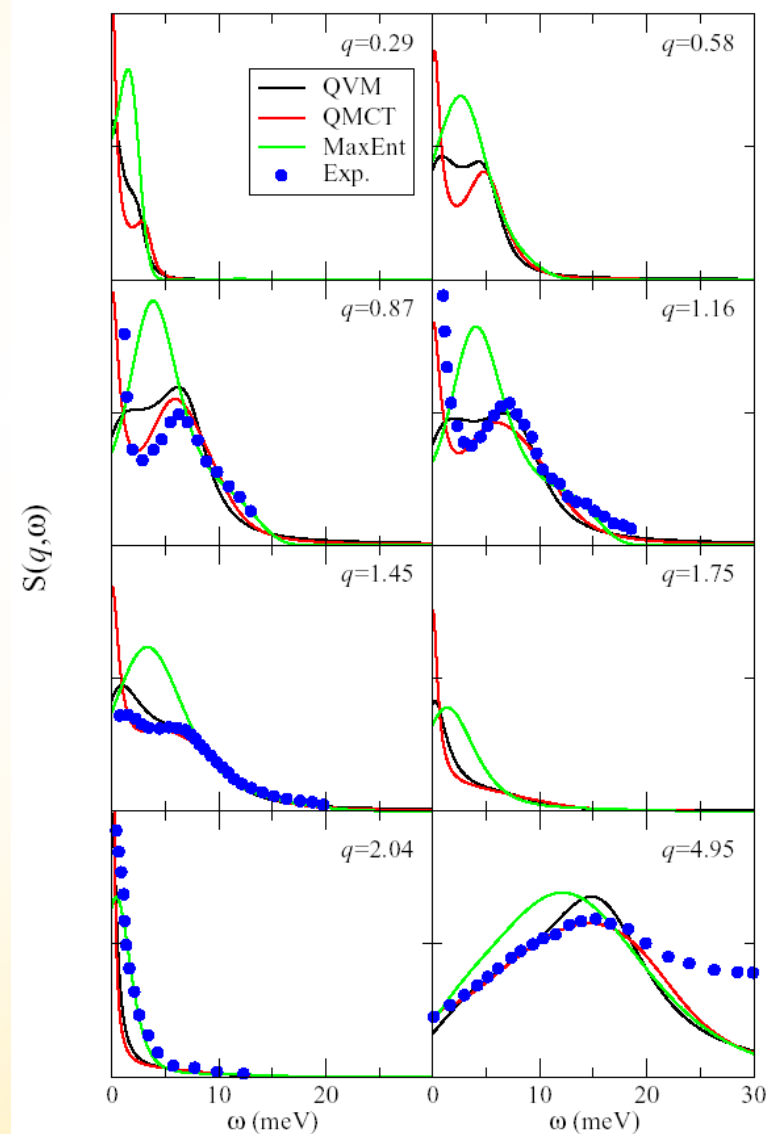


The normalized intermediate scattering function for liquid *ortho*-deuterium. The red curves are results obtained from the QMCT and the green curves are results obtained from an analytic continuation approach (MaxEnt). Left panels show the corresponding memory kernels computed from the QMCT.

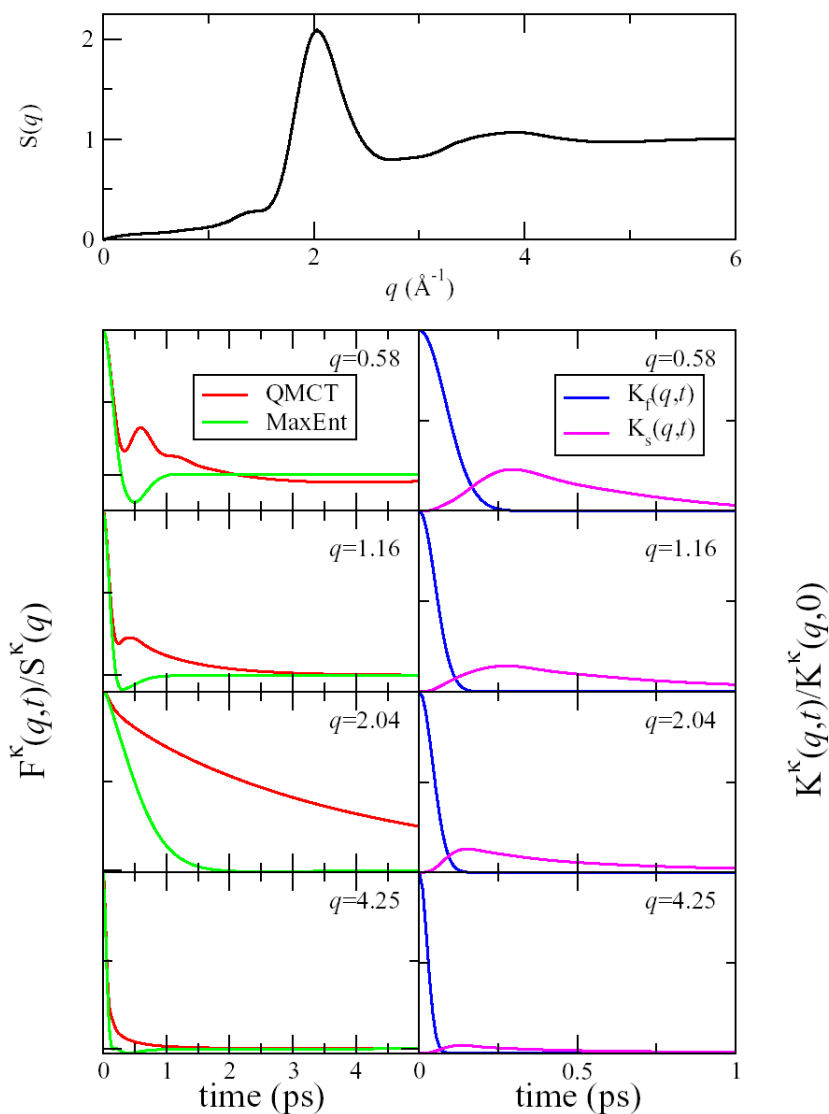
# Dynamic Structure Factor o-D<sub>2</sub>



The normalized dynamic structure factor for liquid *ortho*-deuterium. **Red** – QMCT. **Green** - MaxEnt. **Black** – QVM assuming a single relaxation time. **Blue circles** - experimental results from M. Mukherjee, F. J. Bermejo, B. Fak, and S. M. Bennington, *Europhys. Lett.* **40**, 153 (1997).



# Quantum Liquids p-H<sub>2</sub>



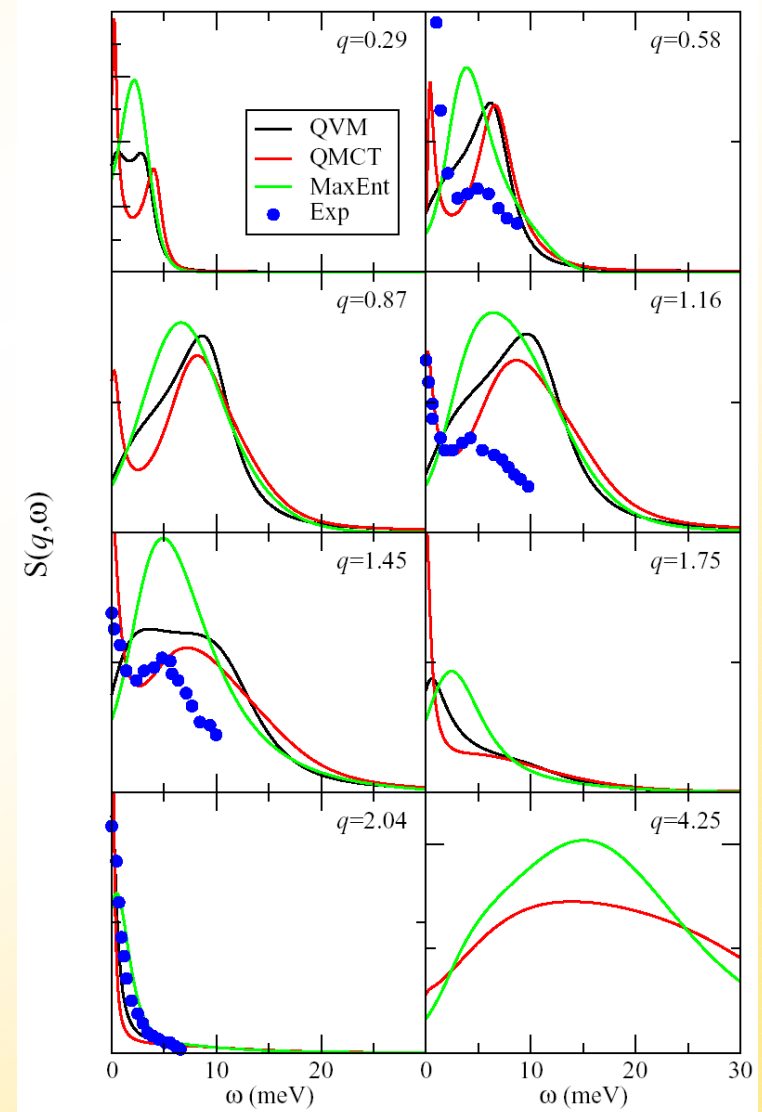
The normalized intermediate scattering function for liquid *para*-hydrogen. The red curves are results obtained from the QMCT and the green curves are results obtained from an analytic continuation approach (MaxEnt). Left panels show the corresponding memory kernels computed from the QMCT.



# Dynamic Structure Factor $p\text{-H}_2$



The normalized dynamic structure factor for liquid *para*-hydrogen. Red – QMCT. Green - MaxEnt. Black – QVM assuming a single relaxation time. Blue circles - experimental results F. J. Bermejo, B. Fak, S. M. Bennington, R. Fernandez-Perea, C. Cabrillo, J. Dawidowski, M. T. Fernandez-Diaz, and P. Verkerk, Phys. Rev. B **60**, 15154 (1999).





Application to Supercooled Glass-  
Forming Quantum Liquids  
(No Experiments, Only Predictions)

# Quantum Glasses



- Can we form a structural quantum glass (superfluidity)?
- Are there any **thermodynamic** signatures that are different for a quantum glass?
- Are there any **dynamic** signatures that are different for a quantum glass?



# Kob-Andersen Model

$$V(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

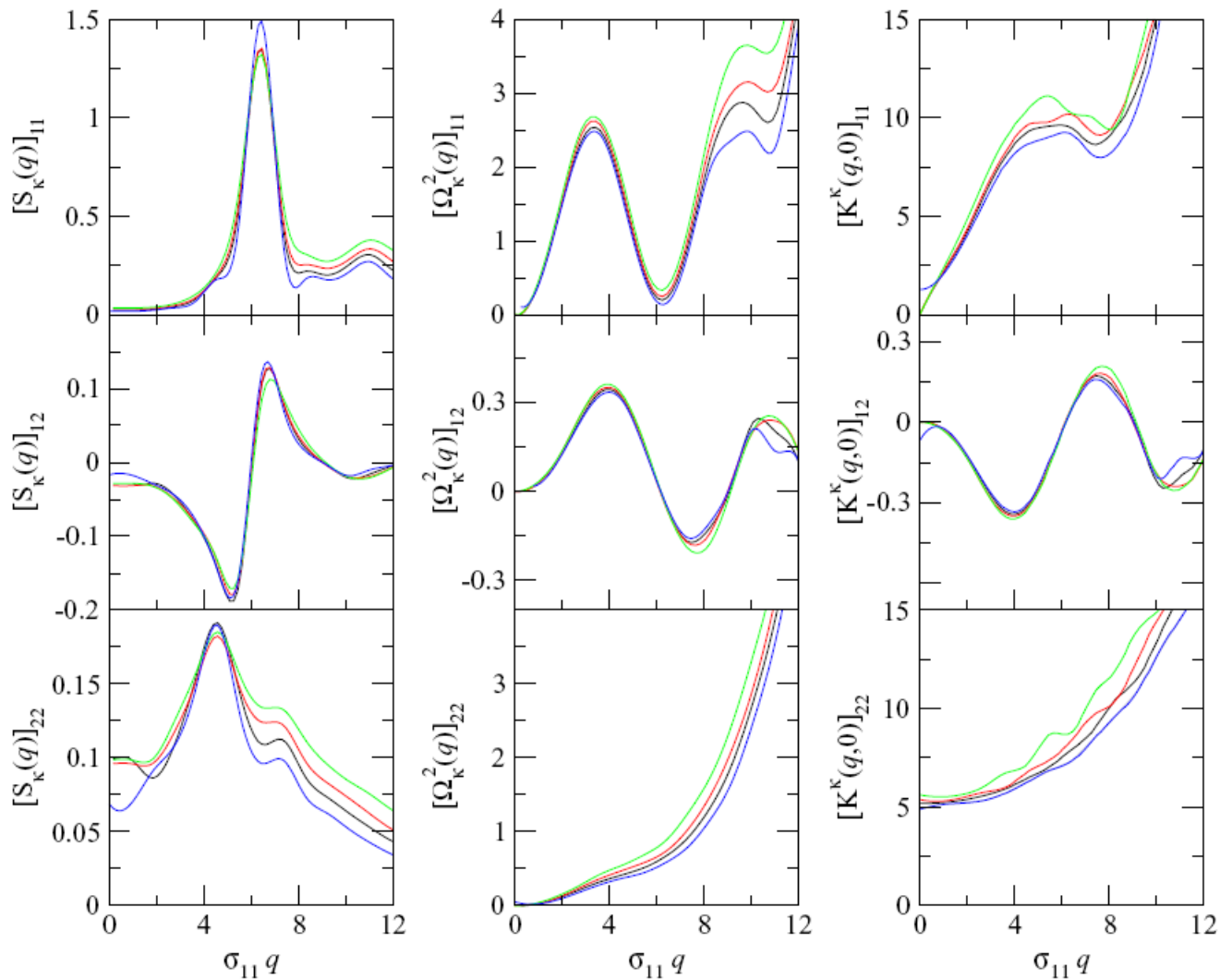
$$\begin{array}{lll} \varepsilon_{AA} = 1 & \varepsilon_{AB} = 3/2 & \varepsilon_{BA} = 1/2 \\ \sigma_{AA} = 1 & \sigma_{AB} = 0.8 & \sigma_{BA} = 0.88 \end{array}$$

$$\hat{n}_{qi} = \sum_{\alpha=1}^{N_i} \exp(iq\hat{r}_{\alpha})$$

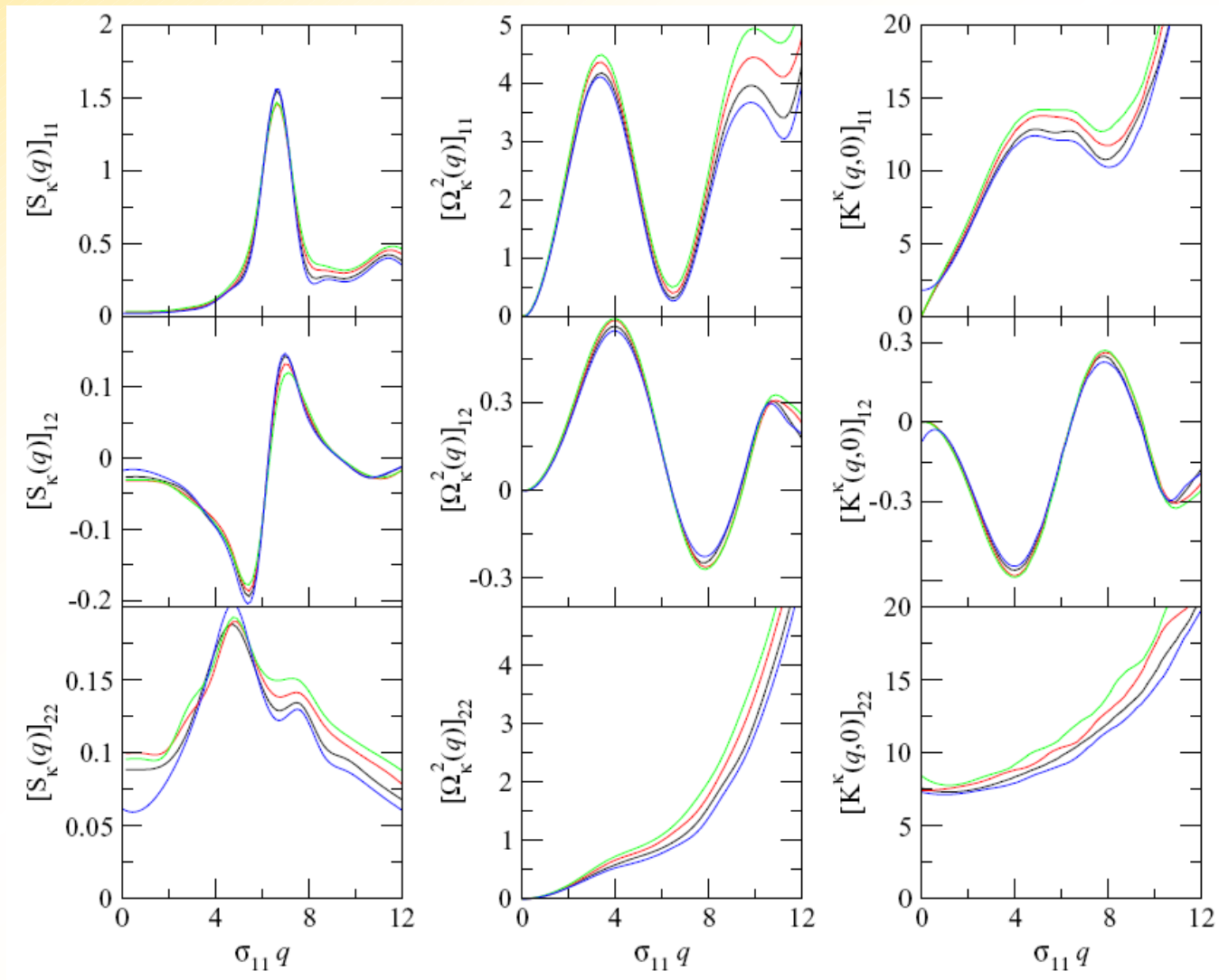
$$F_{ij}^{\kappa}(q, t) = \frac{1}{N} \langle \hat{n}_{qi}^*, \hat{n}_{qj}^{\kappa}(t) \rangle$$

$$\frac{N_A}{N} = 0.8 \quad \frac{N_B}{N} = 0.2 \quad n = 0.8 - 1.0$$

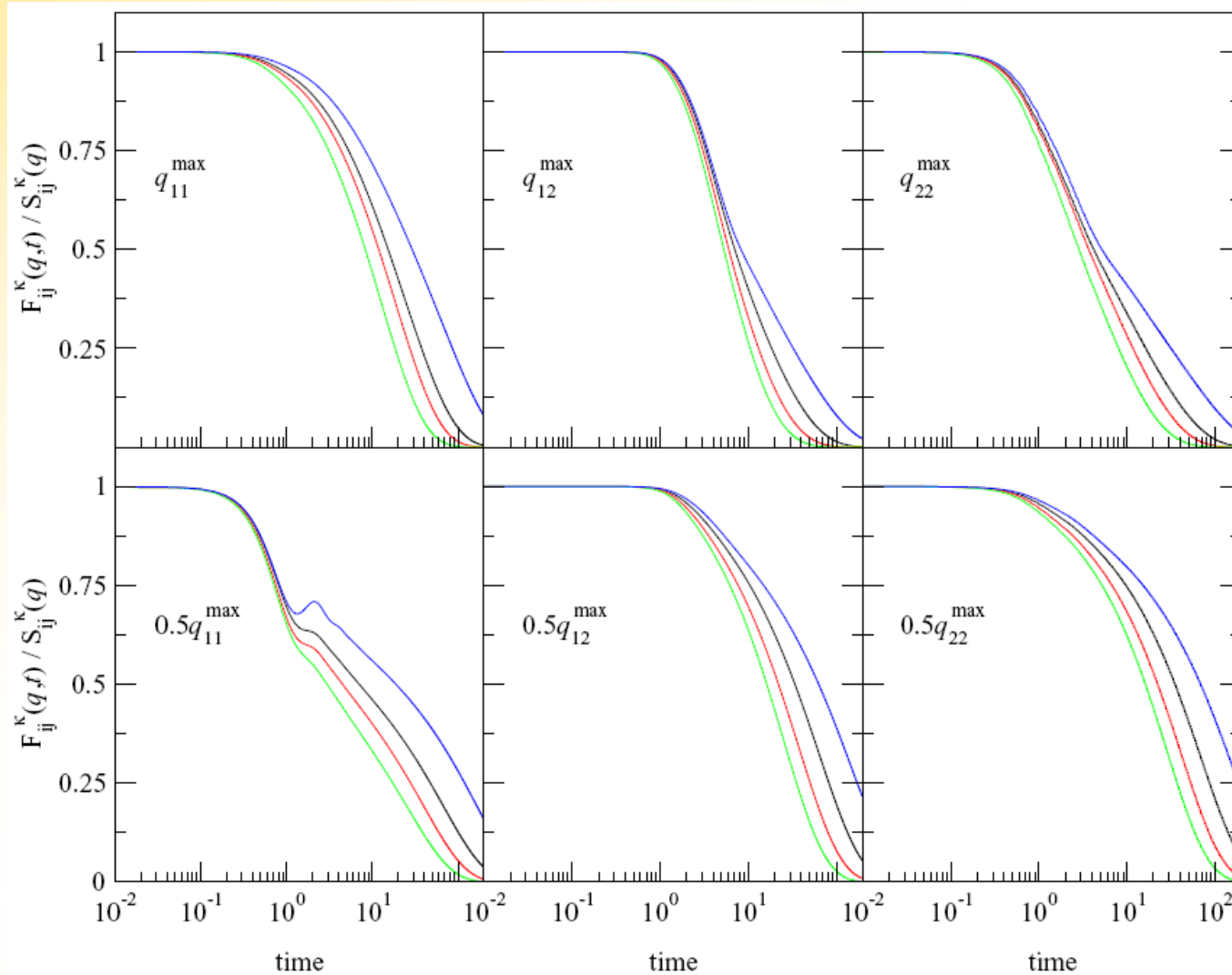
# Structural Input



# Structural Input

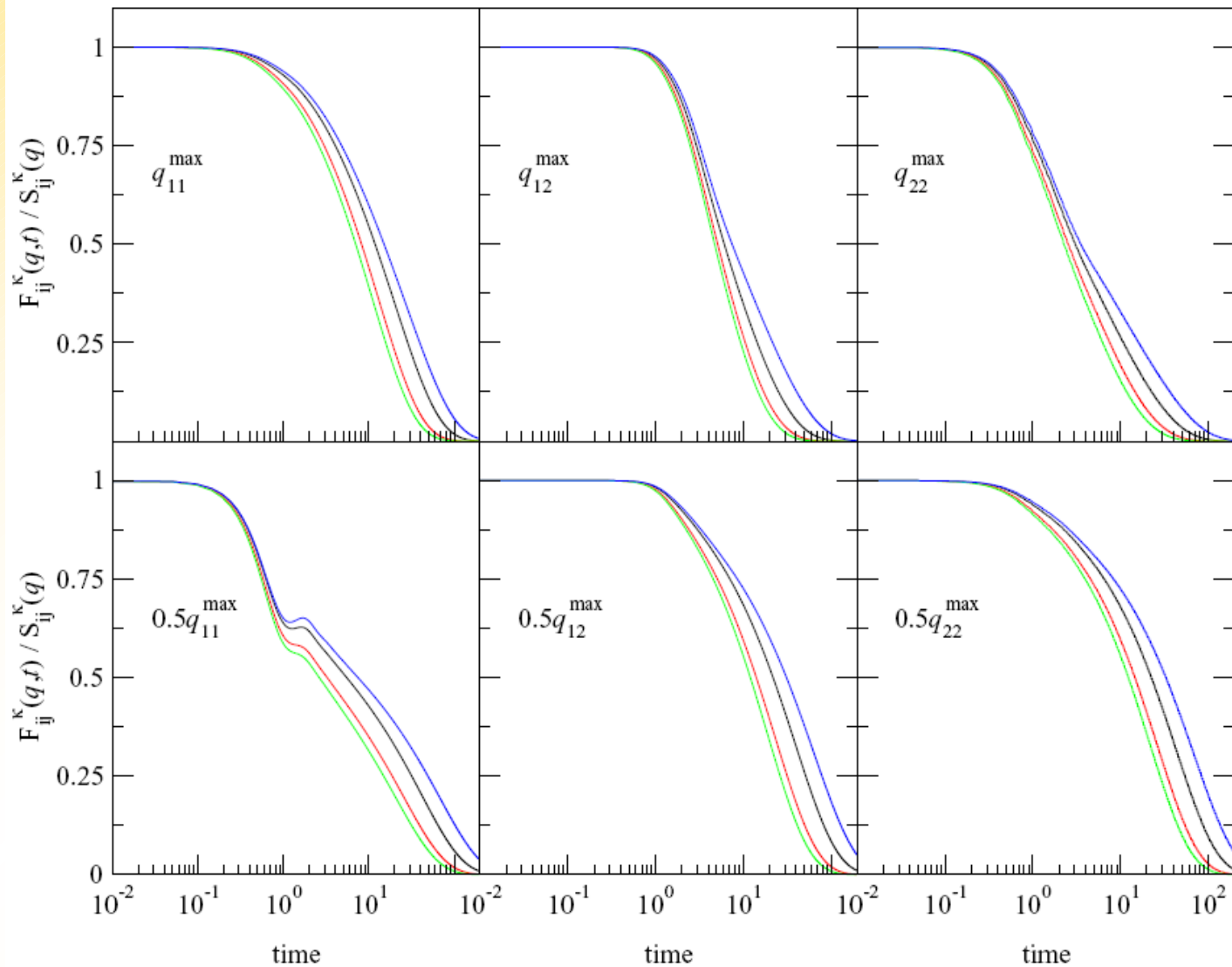


# Intermediate Scattering Function

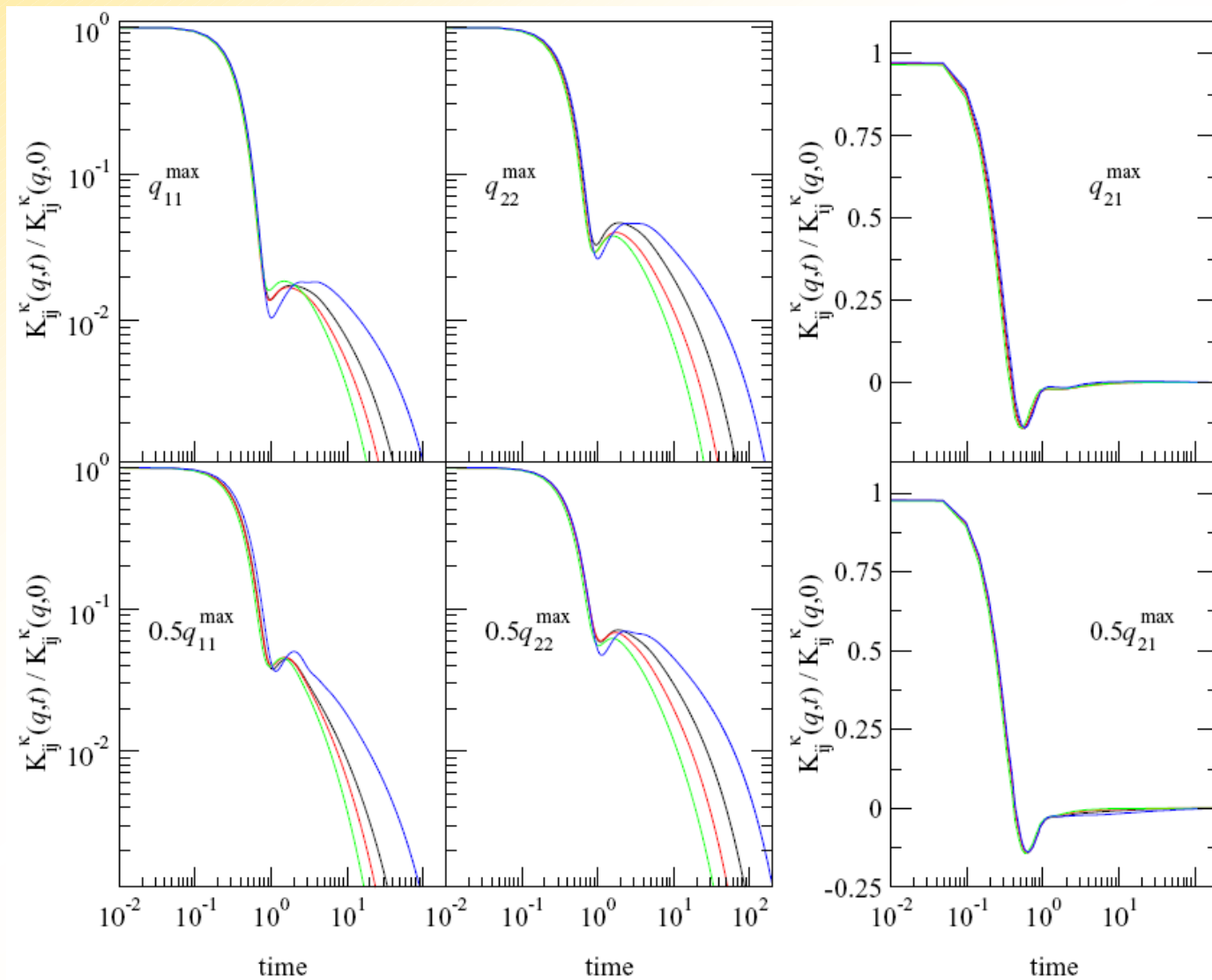




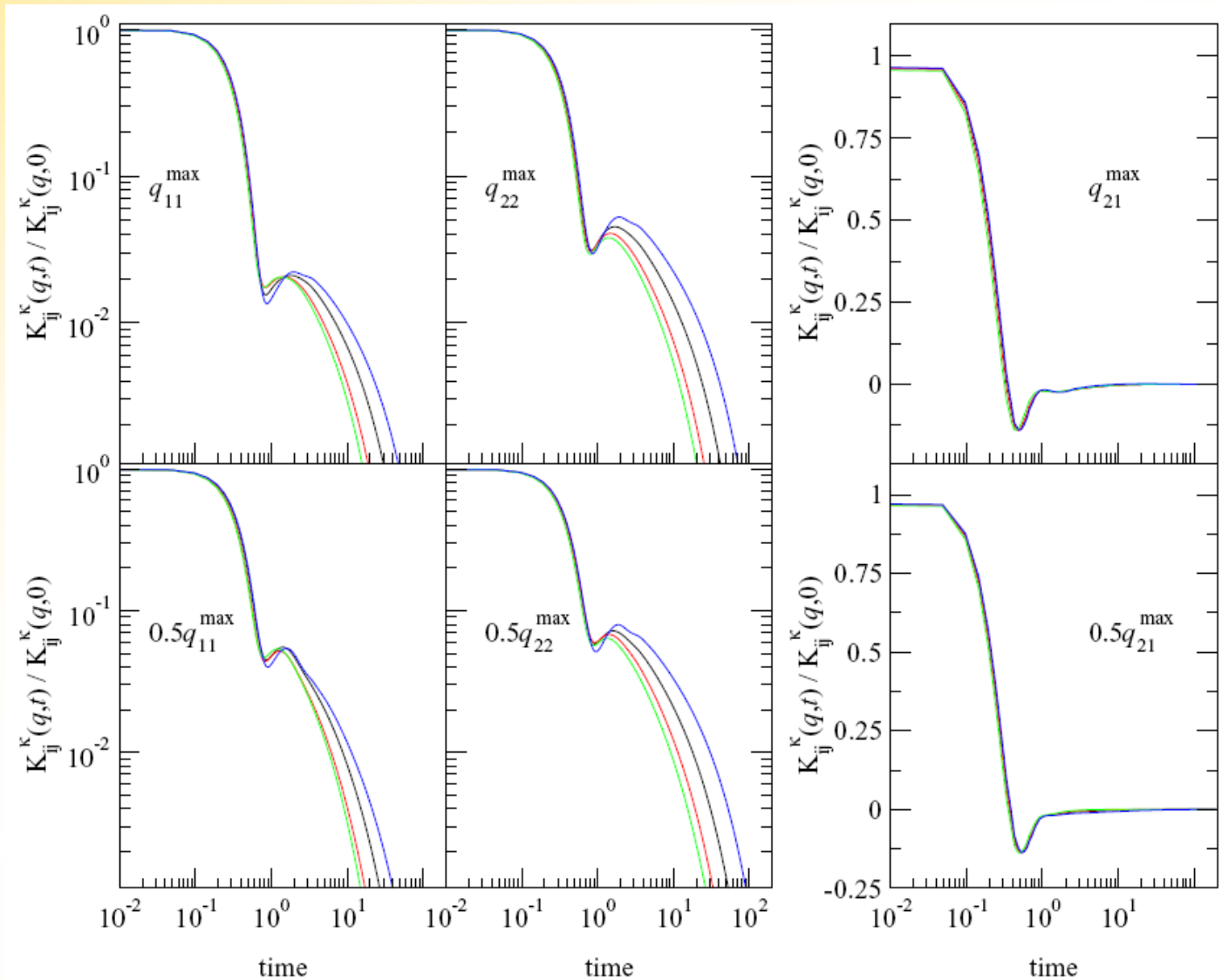
# Intermediate Scattering Function



# Memory Kernel



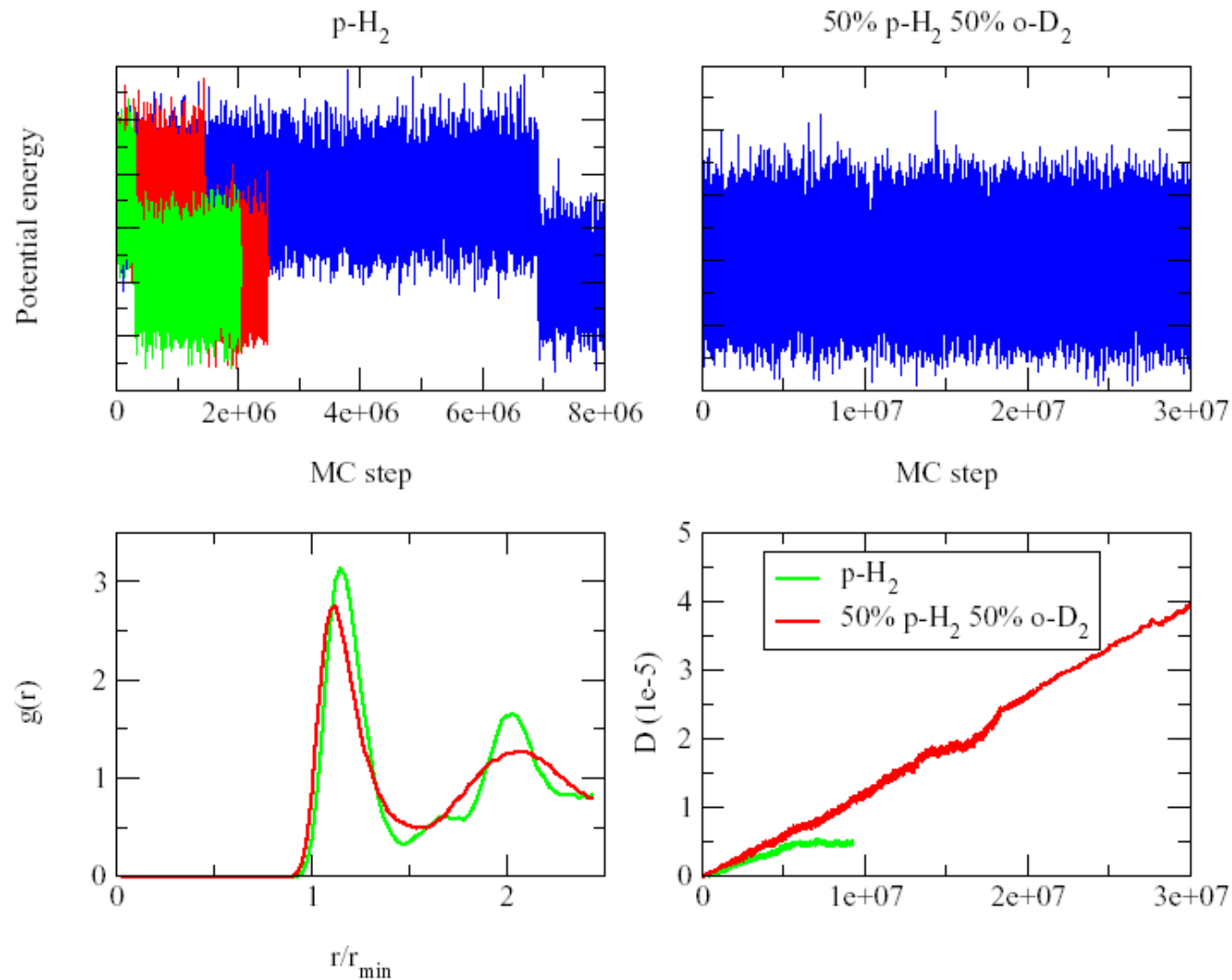
# Memory Kernel



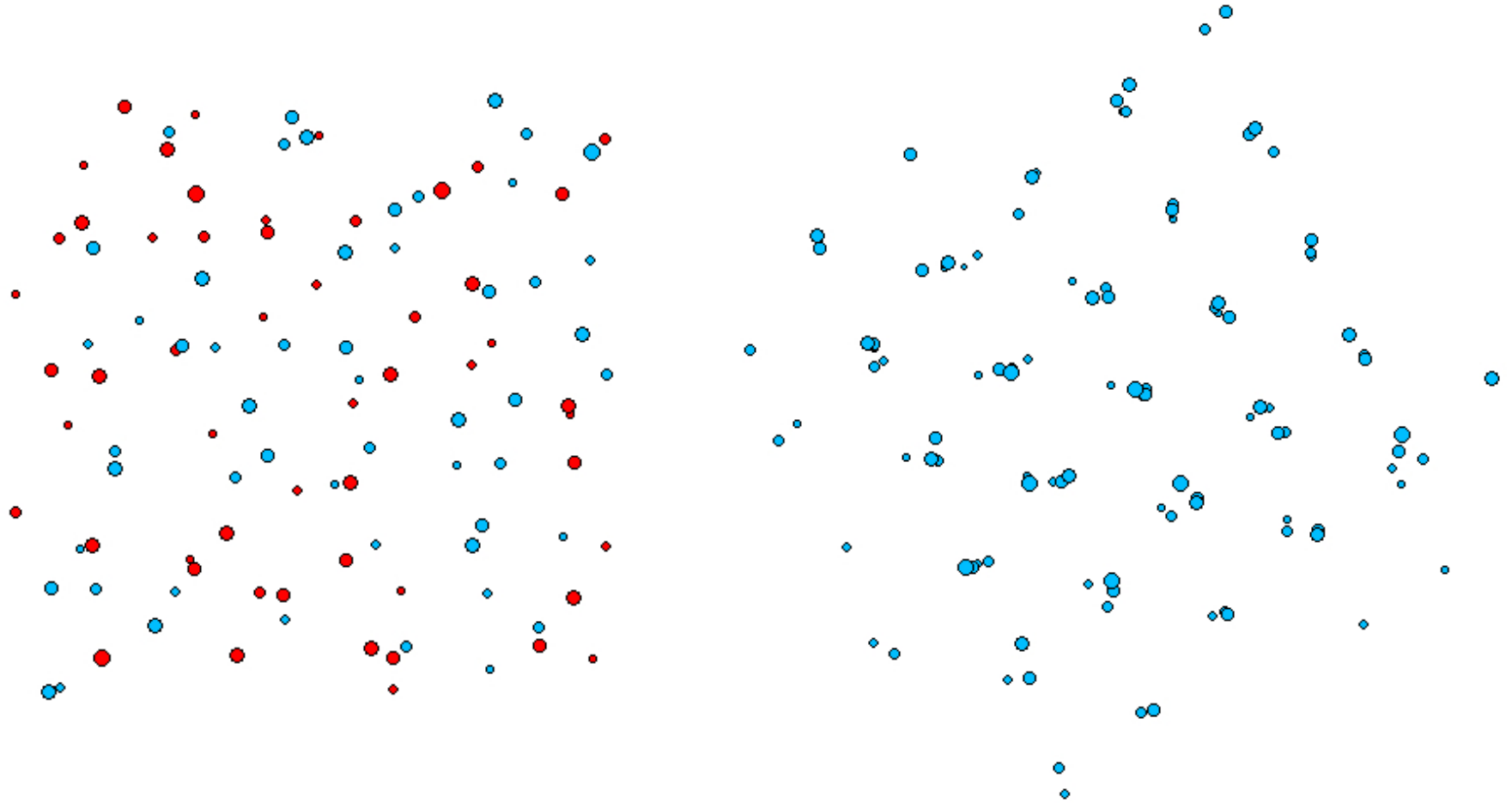


# Experimental Realization

# Mixtures of p-H<sub>2</sub> and o-D<sub>2</sub>



# Centroid Configurations



# QMCT - Conclusions



- **Advantages:** No computation of any kind of **semiclassical** trajectories. Almost any **general** liquid state correlation can be obtained. **Non-Boltzmann** statistics can be described. The **classical limit** can simply be obtained. Describe short and long time phenomena. **Improvements** can be made.
- **But:** Still semi-uncontrolled approximations are made. These approximations can be tested by comparisons to experimental results. Boundary problems cannot be handled (yet).