Time dependent correlations in a supercooled liquid from Nonlinear Fluctuating Hydrodynamics

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(INDO-FRENCH CENTER FOR ADVANCED RESEARCH)

- **Thermodynamic transition and long range correlation**
- **Cooperatively rearranging regions (CRR), Static correlation length.**
- **Length scales related to dynamics. dynamic heterogeneity**

I. Propagating Shear Waves - viscoelasticity

II. Four point correlation functions.

- **Single particle dynamics : Non gaussian parameter**
- **Collective density fluctuations**

Model calculation for a simple liquid using equations of Fluctuating Nonlinear Hydrodynamics.

- **Non-equilibrium dynamics and Modified Stretched exponential relaxation**

Correlation length

$$\langle \delta\psi(\mathbf{x})\psi(\mathbf{x}')\rangle \sim \exp\left[-|\mathbf{x}-\mathbf{x}'|/\xi\right]$$

Divergence of correlation length as the critical temperature is approached.

$$\xi \sim |T - T_c|^{-\nu}$$

Static correlation function

Fluctuation up to correlation length are important in our understanding of the critical phenomena.

Length scales and relaxation times

Adam-Gibbs scenario.

Cooperatively relaxing regions(CRR)

The **number of differnet configurations** a CRR takes is independent of the temperature T and number of particles n(T) involved

$$W_N = \{\nu_c\}^{N/n} \qquad S_c(T) = \frac{1}{N}\ln W_N = \frac{\ln \nu_c}{n(T)}$$

The configurational entropy and n(T) are inversely related.

Relaxation through barrier hopping and activated process

E_B for this process is proportional to n

$$E_B = \frac{\Delta_c}{S_c(T)}$$

$$\tau_\alpha = \tau_0 \exp\left(\frac{\beta\Delta_c}{S_c(T)}\right) .$$

$$n \sim \xi_s{}^d$$

$$\tau_\alpha = \tau_o \exp\left(\frac{B_o \xi_s^d}{k_B T}\right)$$

Length scales related to the dynamics

Spatially heterogenetious dynamics

Molecular dynamic simulations have been used to probe the nature of this dynamics.

Binary Lennard-Jones mixtures.

Mode coupling models consider roles of correlated particle

Motions in the dense liquid.

Effects of structure on the dynamics.

Generally applicable over higher temperture regimes.

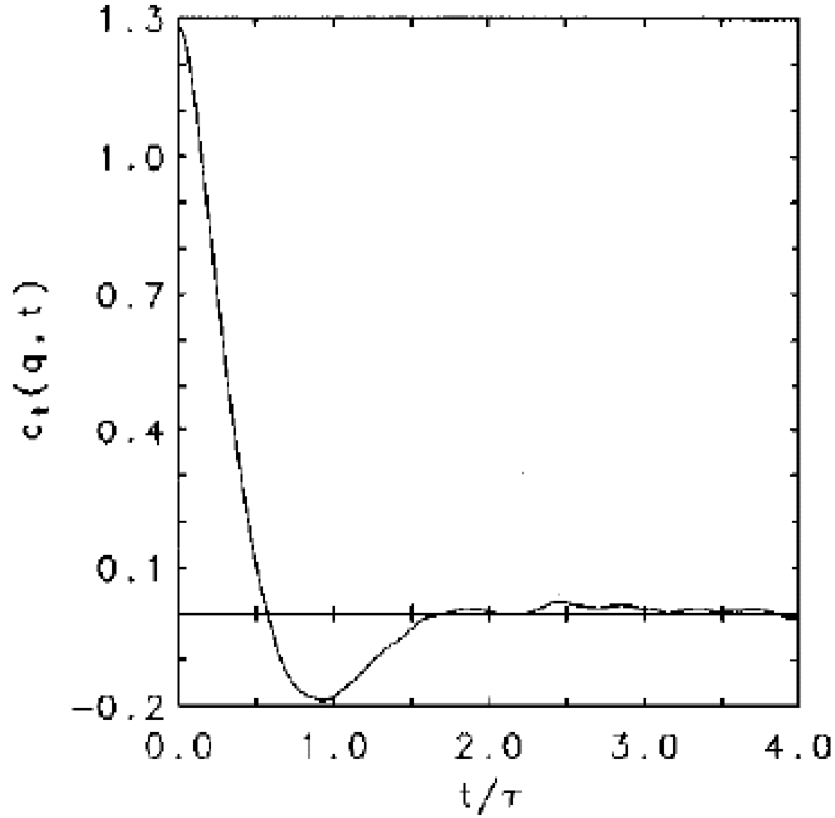
Theoretical models display growing correlationlength.

Propagating Shear Waves

soft sphere mixture simulation

(Mountain, 1997)

- At high frequency the liquid has solid like properties. **SHEAR WAVES**
- **At a given density the propagating shear waves can have a maximum wavelength.**
- This length grows with supercooling.
- A dynamic length scale
- Essentailly **related to the increase of the shear viscosity**



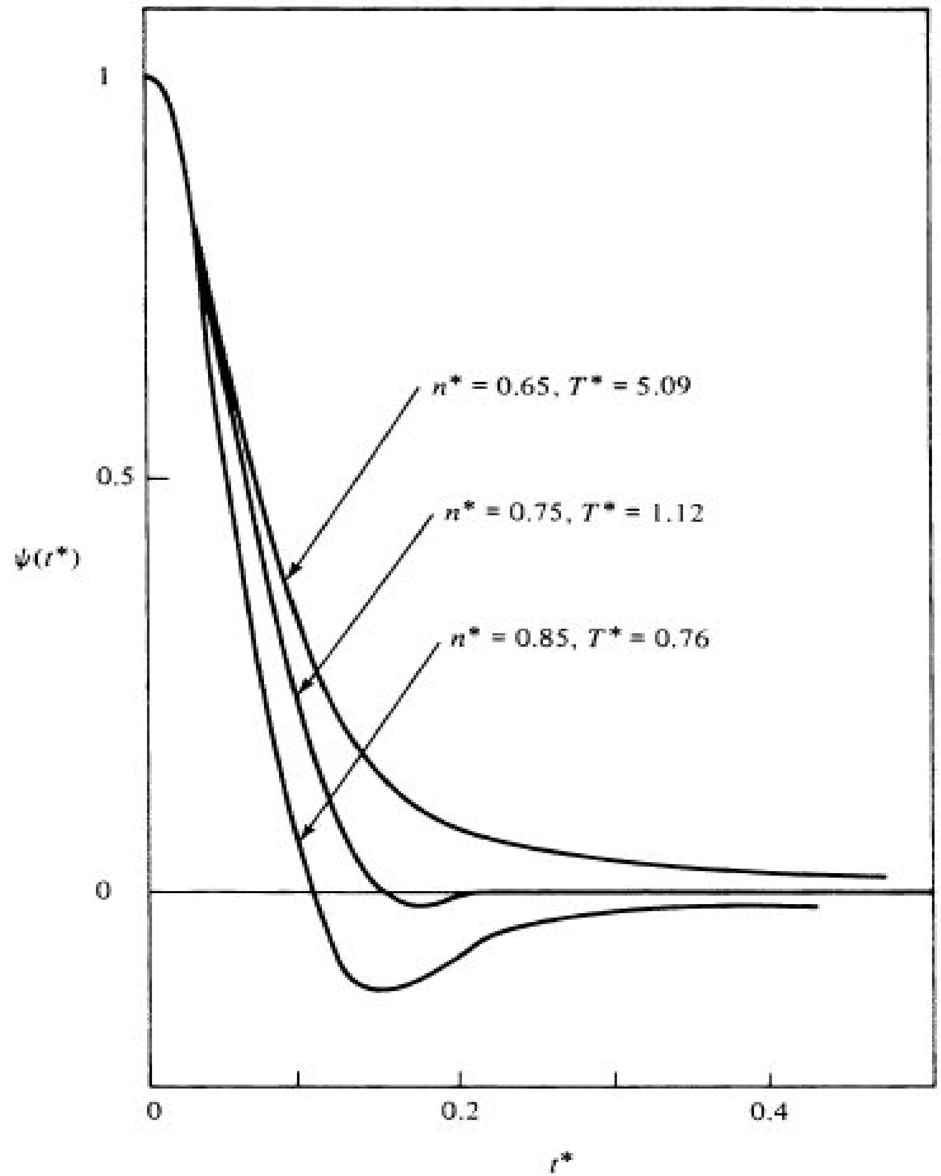
Correlated dynamics of the particles

Mode coupling models.

Cage-effect

Tagged particle velocity auto correlation function

(Levesque and Verlet 1970).



Shear waves

$$\phi_T(q,z) = \frac{1}{z + iq^2\eta_R(q,z)}$$

$$\eta_R(q,z) = \eta_0 + \int dt\,\eta_{\mathrm{MC}}(q,t)e^{izt}$$

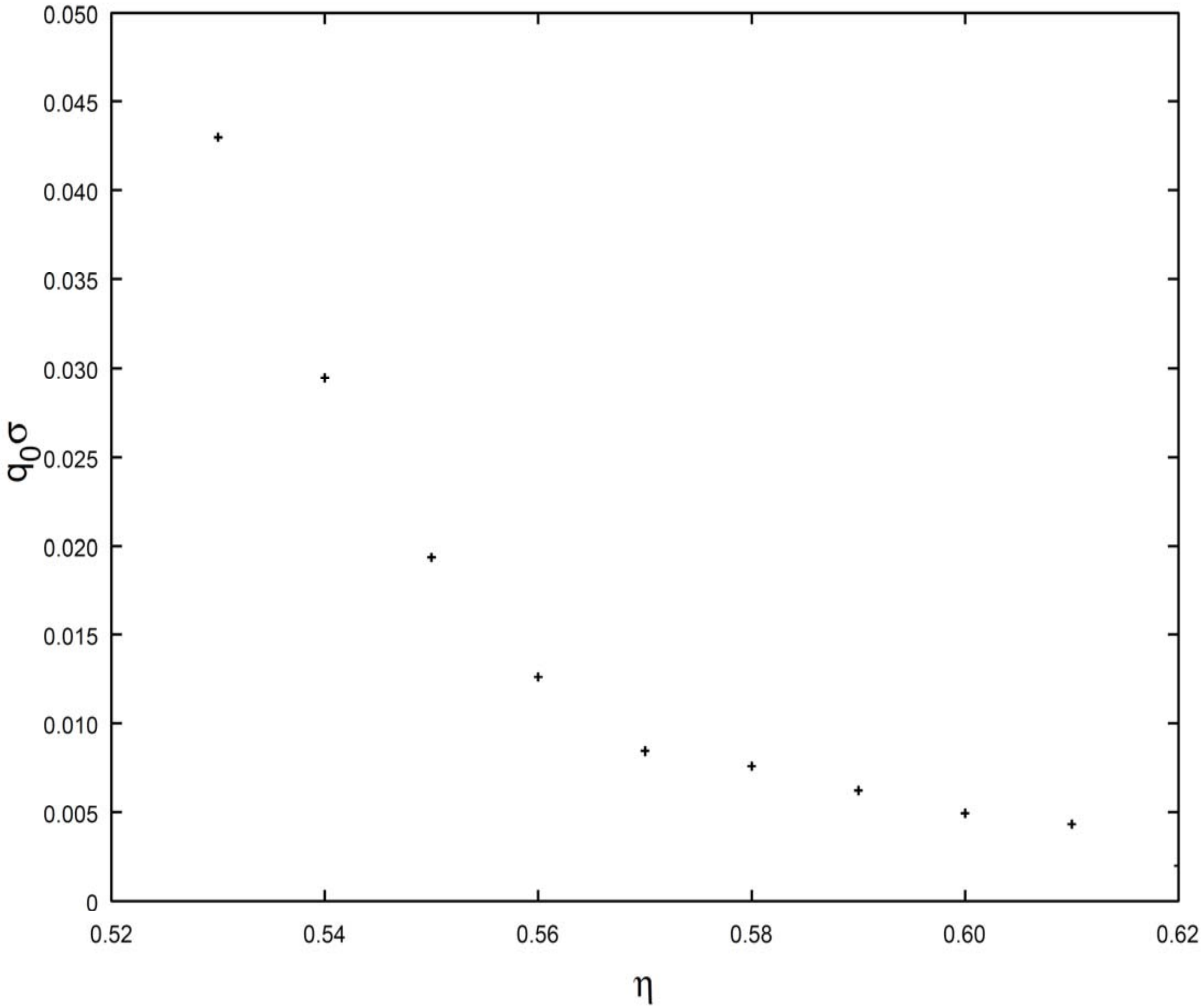
From simple MCT : Dynamic transition at Tc

→ **Diverging shear viscosity**

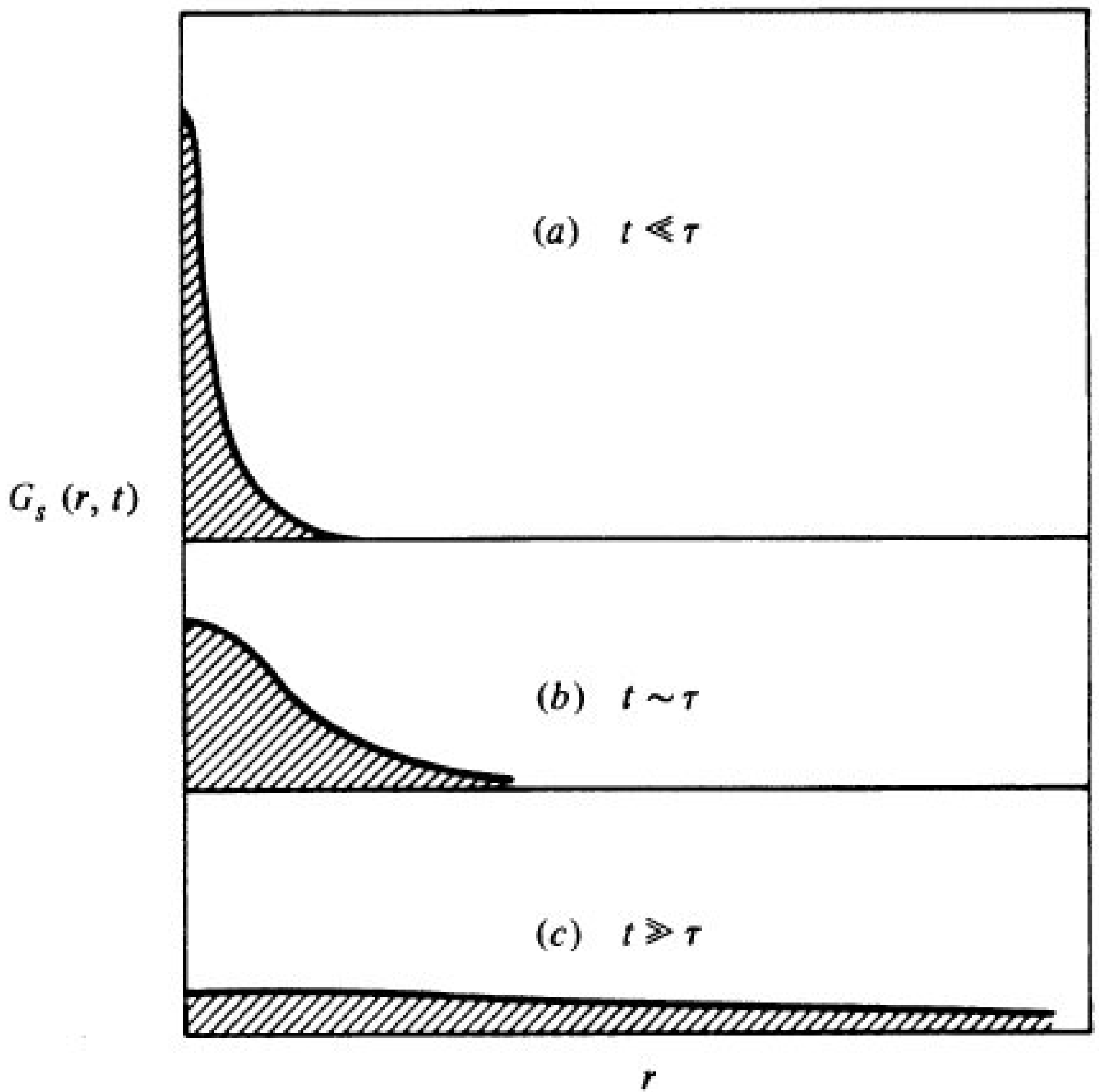
Approaching the ideal transition of the MCT this length scale diverges diverges. Viscoelastic behavior using structure

Ahluwalia and Das, 1998, Das, 1999.

Maximum wave number q_0 for propagating shear waves



Tagged particle correlation



Single Particle dynamics

Including mode coupling effects

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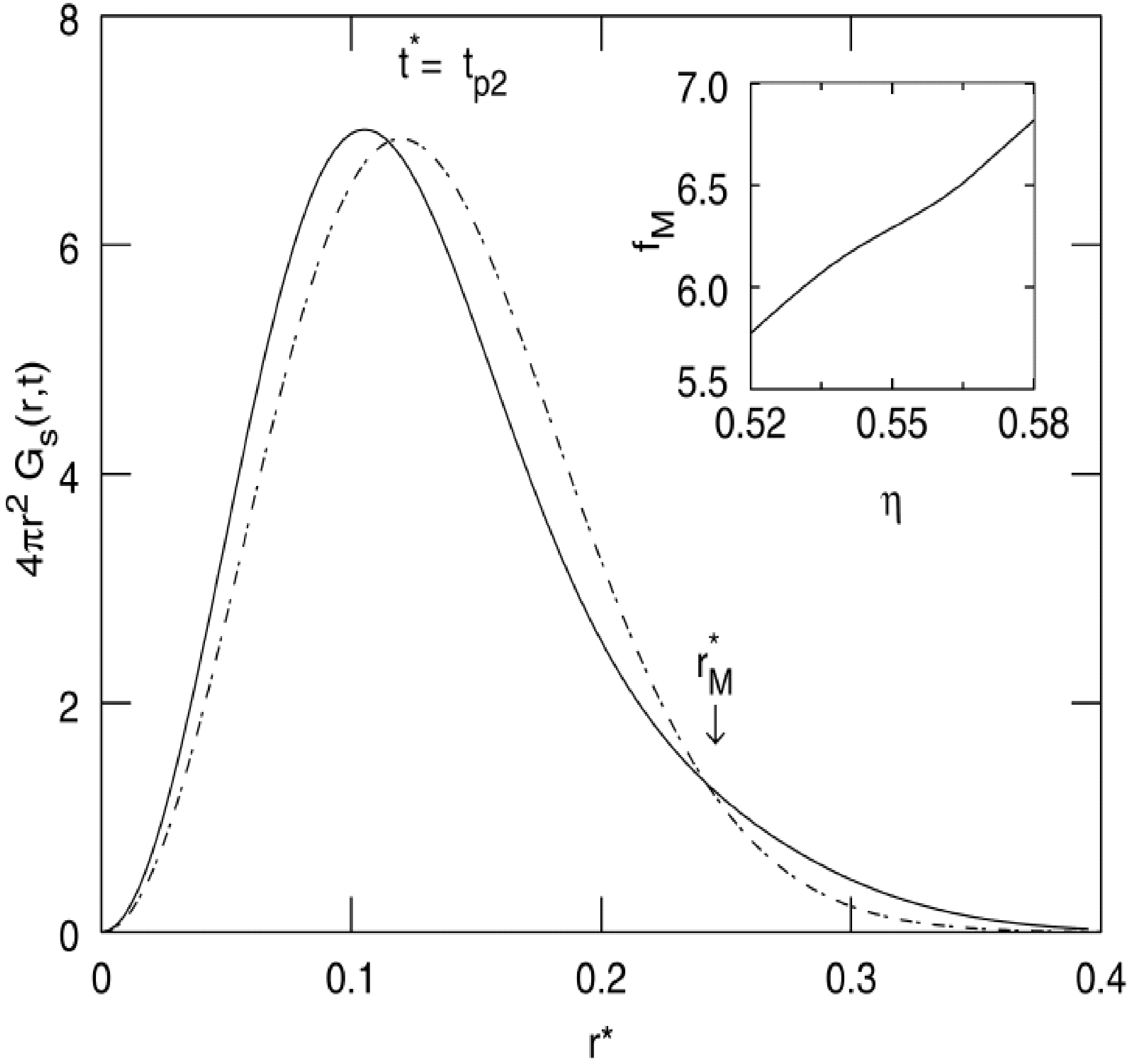


Non-gaussian Parameter

$$\alpha_2(t) = \frac{3}{5}\frac{\langle r^4(t)\rangle}{\langle r^2(t)\rangle^2} - 1$$

Related to four point functions

$$F_s(k,t) = \exp\left[-k^2\varrho_1(t) + k^4\varrho_2(t) - k^6\varrho_3(t) + \ldots\right]$$

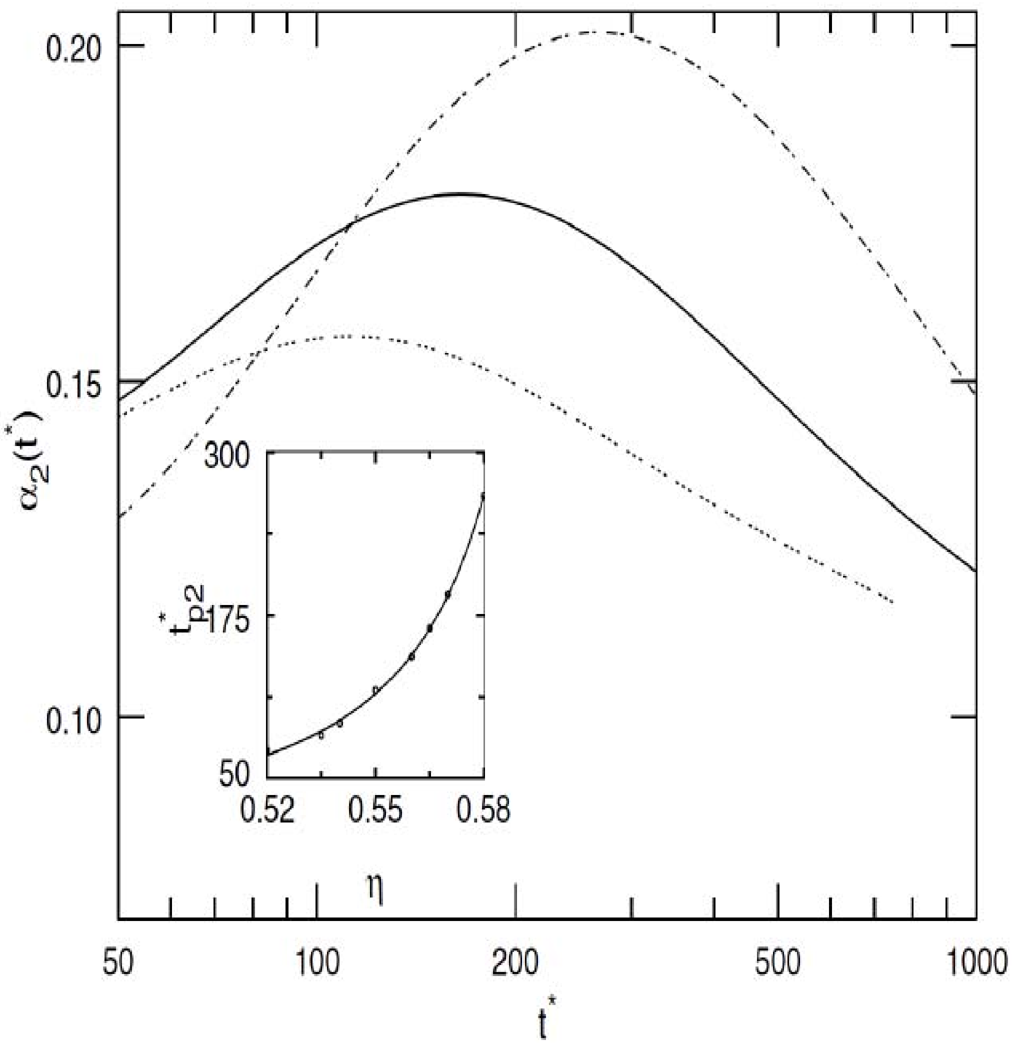
$$\Delta_k(t) = k^2\varrho_1(t) \longrightarrow$$

$$= e^{-\Delta_k(t)}\left[1 + \frac{\Delta_k^2(t)}{2!}\alpha_2(t) - \frac{\Delta_k^3(t)}{3!}\{\alpha_3(t) - 3\alpha_2(t)\}\ldots\right]$$

$$\varrho_1(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 < u(t_1)u(t_2) >$$

$$\varrho_2(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 < u(t_1)u(t_2)u(t_3)u(t_4) > -\frac{1}{2}\varrho_1^2(t)$$

.....



0.20
0.15
0.10
$\alpha_2(t^*)$
50
100
200
500
1000
t^*
300
175
50
t^*_{p2}
0.52
0.55
0.58
η

Dynamics

Microscopic picture : **Classical system of N particles.**

N large : many degrees of freedom.

Kinetic Theory

- **Transport properties ← interaction of the particles.**
- **Valid for Low densities**

Molecular Dynamics simulations

Small number of particles – microscopic dynamics

Periodic boundary conditions.

Dynamics of a set of slow modes

Complex dynamics with many degrees of freedom

Choice of the slow modes

Conservation laws

Goldstone modes

Brownian particle

Dynamics in the projected space of slow modes

Orthogonal space of fast modes

Mori-Zwangig Projection operator scheme

The nonlinear Langevin equation

The bare transport coefficicsnts related to the noise correlation.

$$\frac{\partial \hat{\phi}_i(t)}{\partial t} = V_i[\hat{\phi}] - \sum_j L^0_{ij} \frac{\partial F}{\partial \hat{\phi}_j} + \theta_i(t) \quad ,$$

$$< \theta_i(t)\theta_j(t') >= 2k_B T L^0_{ij} \delta(t - t')$$

Time correlation of slow modes

$$C_{ab}(t, t') = < \delta\hat{\psi}_a(t)\delta\hat{\psi}_b(t') >$$

Equilibrium average

Correlation of density fluctuations.

Dynamic structure factor

Average over initial conditions

Average over noise in stochastic equations

Equations of Nonlinear Fluctuating Hydrodynamics

Brownian motion of a single particle : The velocity of a big particle (large mass) is identified as the slow variable with the equation of motion $\partial_t \mathbf{v}(t) = -\zeta \mathbf{v}(t) + f(t)$

- **Isotropic liquid**

Dynamics in terms of the slow modes due to conservation laws.

- Mass, Momentum and Energy density
- Fluctuations around the Equilibrium state

Isotropic Liquid

Mass density $\rho(x,t)$

Momentum density $g(x,t)$

Fluctuating equations for the slow variables

$$\frac{\partial \rho}{\partial t} + \nabla.\mathrm{g} = 0$$

$$\frac{\partial g_i}{\partial t} = -\rho \nabla_i \frac{\delta F_U}{\delta \rho} - \sum_j \nabla_j \left(\frac{g_i g_j}{\rho}\right) + \sum_j L^o_{ij} \frac{g_j}{\rho} + f_i \ .$$

Plausible generalizations of the laws of hydrodynamics

Low density : linear equations of motion are sufficient for describing the dynamics

Supercooled liquids : Cooperative motion of the liquid particles.
Coupling of the hydrodynamic modes.

.

Mode coupling effects

- **Collective effects through coupling of slow modes**

$$\lim_{q\to 0}\frac{\partial}{\partial t}a_i(\mathbf{q},t)=0.$$

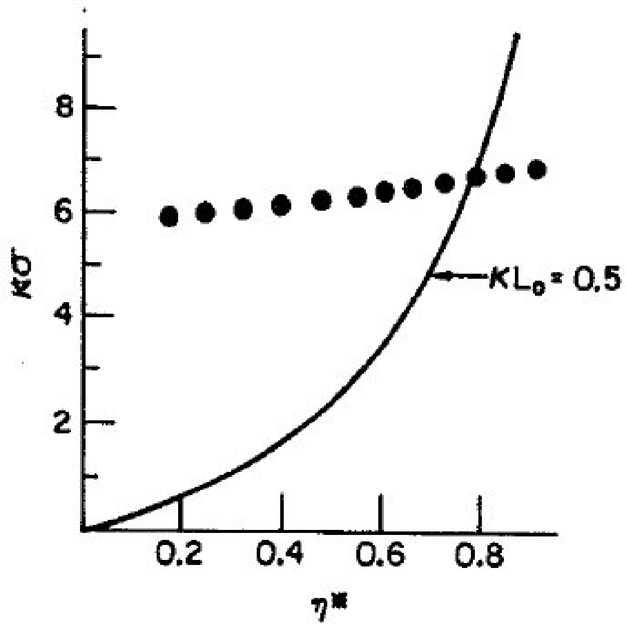
$$\lim_{q\to 0}\frac{\partial}{\partial t}\int d\mathbf{x}e^{i\mathbf{q}.\mathbf{x}}a_i^2(\mathbf{x},t)=2\int\frac{d\mathbf{k}}{(2\pi)^3}i[\mathbf{k}.\mathbf{J}_{a_i}(\mathbf{k},t)]a_i(-\mathbf{k},t)$$

$$\partial_t a_i+\nabla.\mathbf{J}_{a_i}=0,$$

Generalized Hydrodynamics

- At high densiy the mean free path is very small.
- Ensures validy of the hydrodynamic equations to short wavelenghts

Black dots :position of first peak of S(k)



Effect of nonlinearities

Renormalization of transport coefficients due to nonlinearities in the equations for the slow modes.

- **Slow dynamics results from a feed back effects of coupled density fluctuations.**
- **Self-consistent mode-coupling theory (MCT)**
- **Signatures of a dynamic transition**

- **Describes the dynamics well above the calorimetric glass transition temperature Tg**

Corrections due to nonlinearities are calculated low order in a perturbation series.

Numerical Solution of the Stochastic Equations

- Simplest set of equations involving the density $\rho(x,t)$ and the momentum $g(x,t)$
- Discrete cubic lattice of small size 20^3
- Periodic boundary conditions
- Gaussian white noise

Noise correlation is described in terms of the dissipative tensor involving the shear and the longitudinal viscosity

Lennard-Jones Potential：

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Rescaled variables

$$\rho(x) = [mh^{-3}]n(x) \qquad g(x) = [\sqrt{m\epsilon}h^{-3}\alpha]j(x)$$

- Length is scaled with the unit h of lattice constant and time with the Lennard-Jones unit.

- Two length scales σ and the lattice constant h.
- We choose the ratio $\alpha \neq 1$ to avoid crystallization.

FLUCTUATING EQUATIONS

Continuity Equation

$$\frac{\partial}{\partial t} n(x,t) + \nabla . j(x,t) = 0$$

Generalized Navier-Stokes Equation

$$\frac{\partial}{\partial t} j_i(x,t) + \nabla_i \delta n(x,t) + n(x,t) \nabla_i f(x,t) + L^0_{ik} v_k(x,t) = \theta_i(x,t)$$

Velocity or current field

$$v_j(x) = j_j(x)/n(x)$$

The non local function f(x,t) :

$$f(x,t) = \int d^3x c(x-x') \delta n(x',t)$$

Gaussian white noise.

$$< \theta_i(x,t) \theta_j(x',t') >= 2T^* L^0_{ij} \delta(x-x') \delta(t-t')$$

Bare transport matrix L

$$L^{ij}_o = (\zeta_0 + \eta_0/3) \delta_{ij} \nabla^2 + \eta_0 \nabla_i \nabla_j$$

The Gaussian noise correlation is obtained in terms of bare transport coefficients for the system.

Bare transport matrix is adjusted so that the short time dynamics agrees with simulations.

The density and momentum fields are stored at the lattice points.

Results at suitably chosen time bins are saved to compute correlation functions.

Both equilibrium and Non equilibrium correlations are studied

Wave-vector independent models (Mazenko and Valls)

Wave-vector dependent models for hard sphere systems (Dasgupta and Valls)

- **Instability due to Negative density**

$$< \theta_i(x,t)\theta_j(x',t') > = 2T^*\lambda L^0_{ij}\delta(x-x')\delta(t-t')$$

Coarse graining of the density field :

No of particles in a small volume at time t

$$\int_{\triangle V} dx\, \rho(x,t)$$

The density is updated at each site in a manner

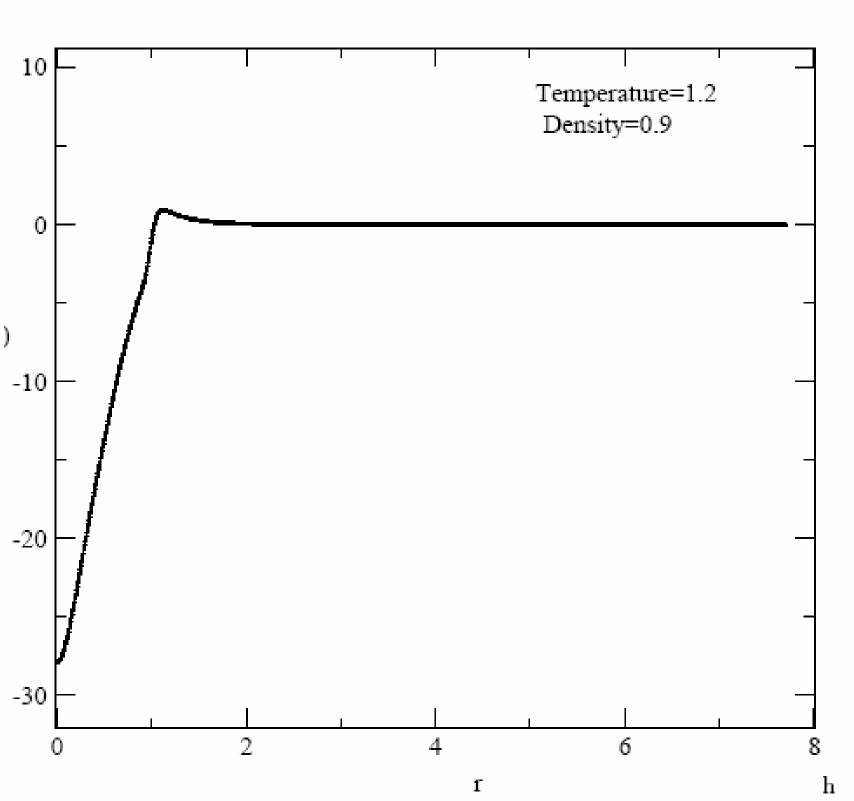
Total density in a cell remains same

Calculation of f(x,t)

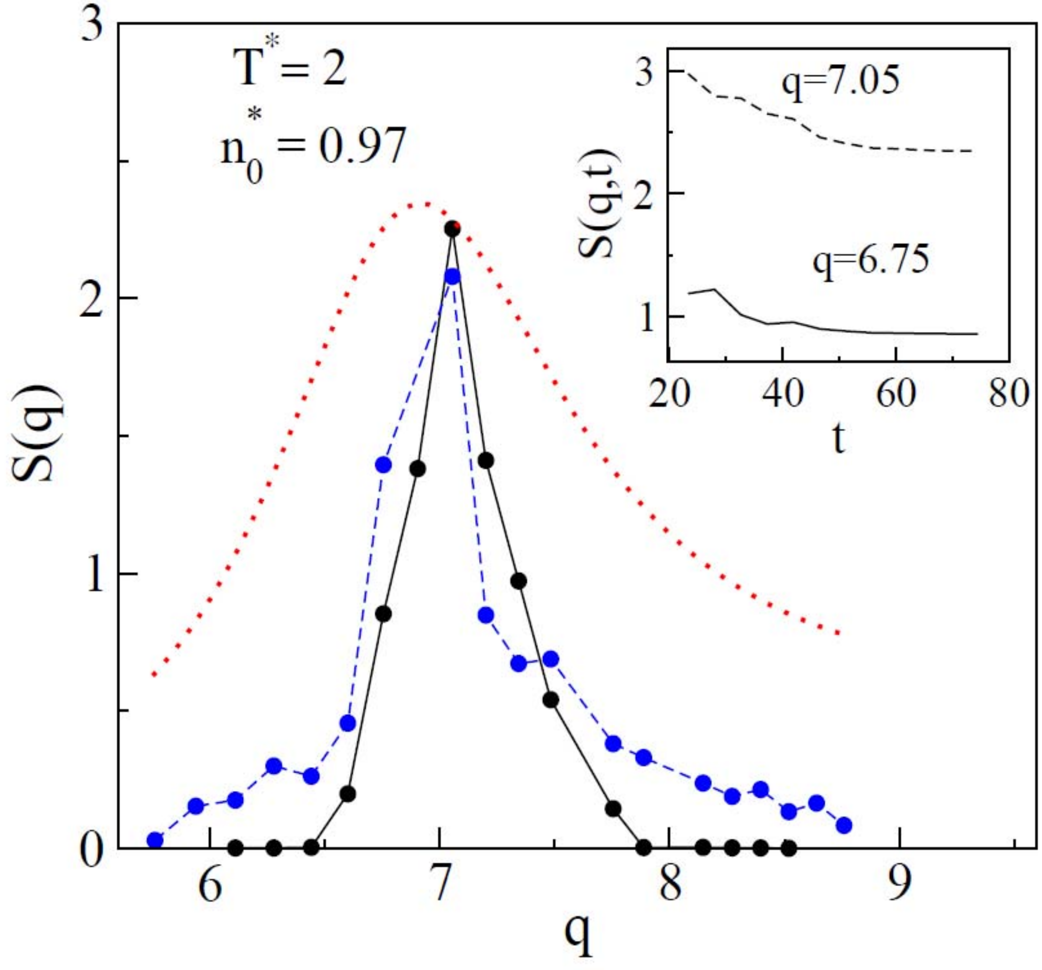
split the integral → sum (concentric shells)

$$f(x,t) = h^3 \sum_i c(R_i)\left[\sum_{\mathbf{R}_i^\alpha} \delta n(\mathbf{R}_i^\alpha, t)\right]$$

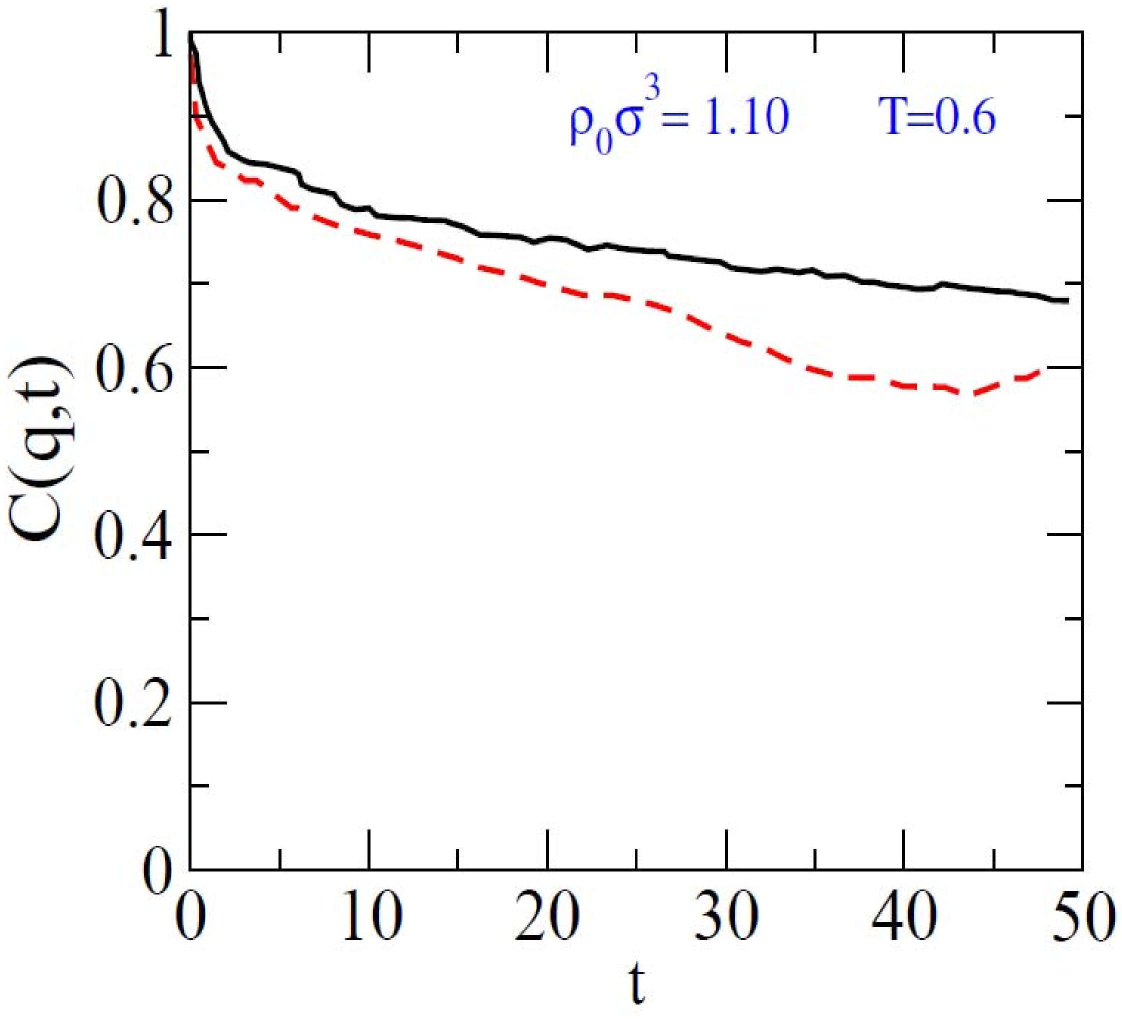
c(R) is the direct correlation function relating to the thermodynamic property of the liquid.



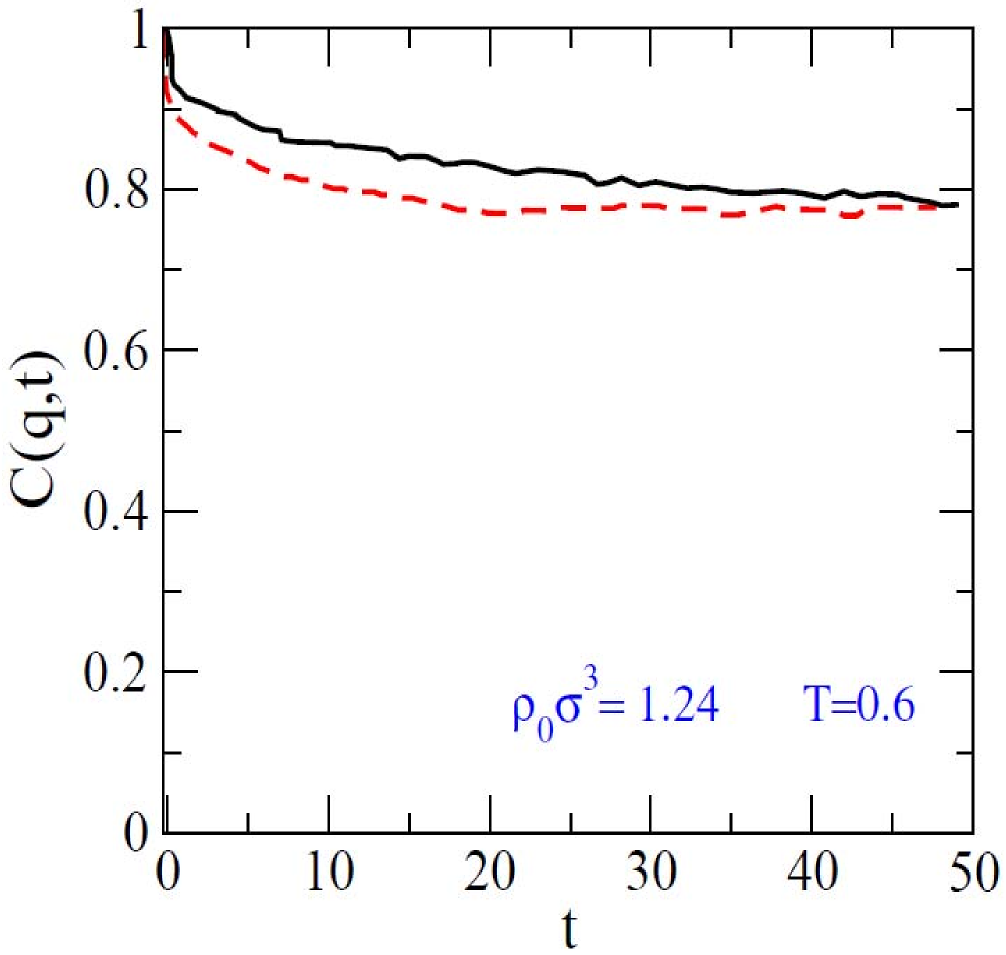
The Static Structure factor



Comparison with MD simulations



Comparison with MD simulations



Generalized Navier-Stokes Equation

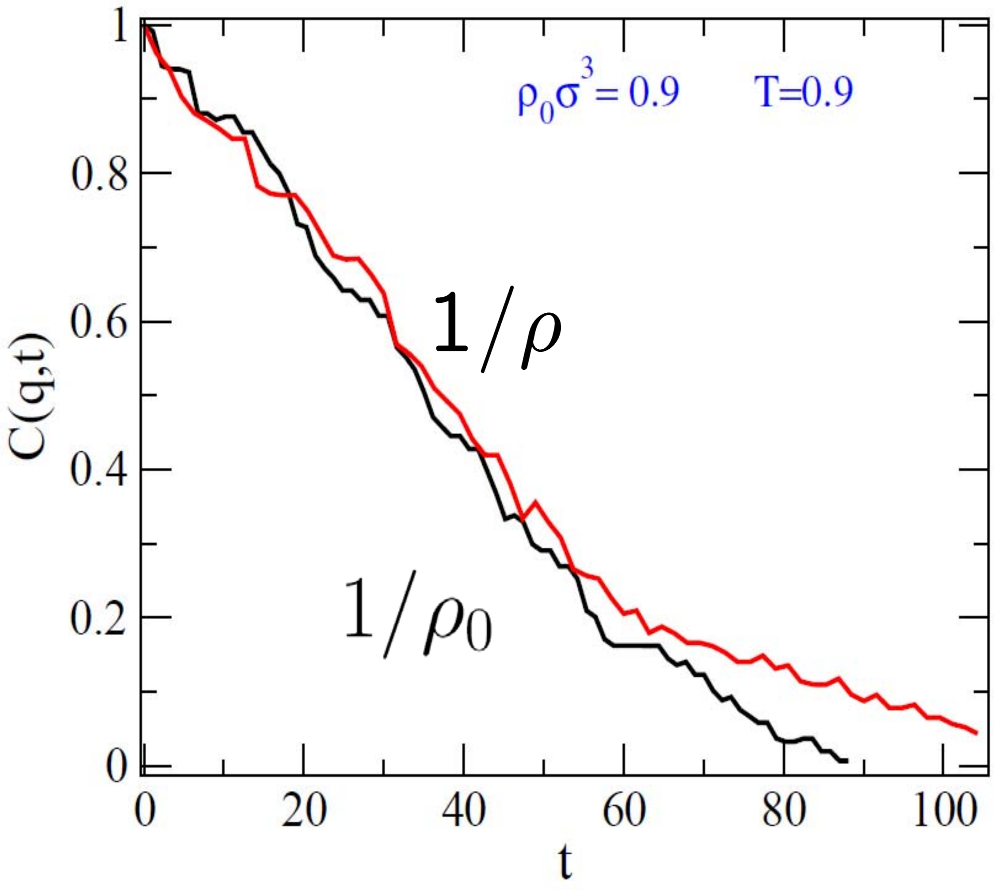
$$\frac{\partial}{\partial t} j_i(x,t) + \nabla_i \delta n(x,t) + n(x,t)\nabla_i f(x,t) + L^0_{ik} v_k(x,t) = \theta_i(x,t)$$

$1/\rho$ nonlinearity in the dissipative term is essential in restoring the ergodicity in the system (Das and Mazenko, 1986)

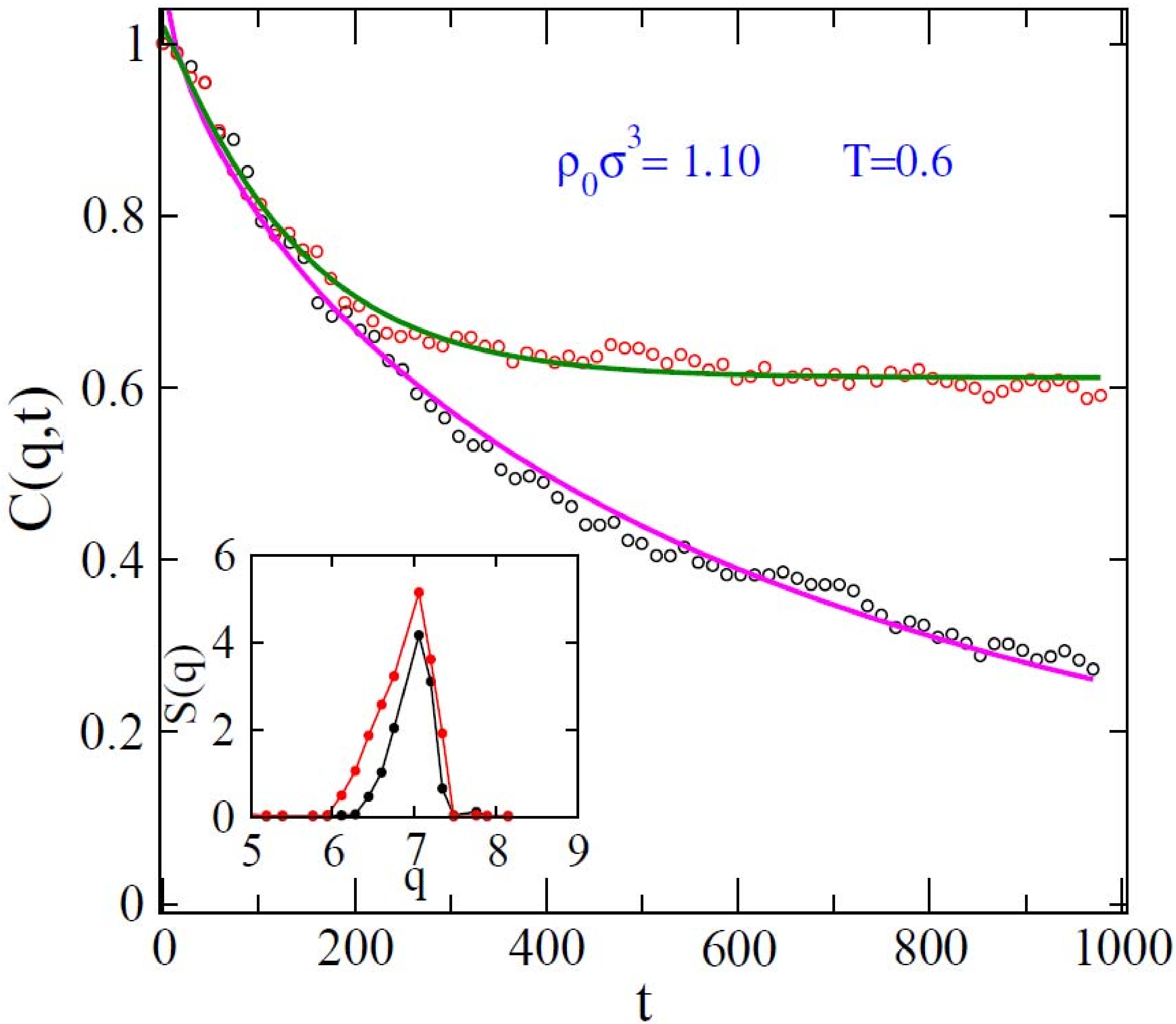
We replace the $1/\rho$ in the current v_k by $1/\rho_0$

The density nonlinearity in the reversible pressure term is kept unchanged.

At low density the two cases are similar

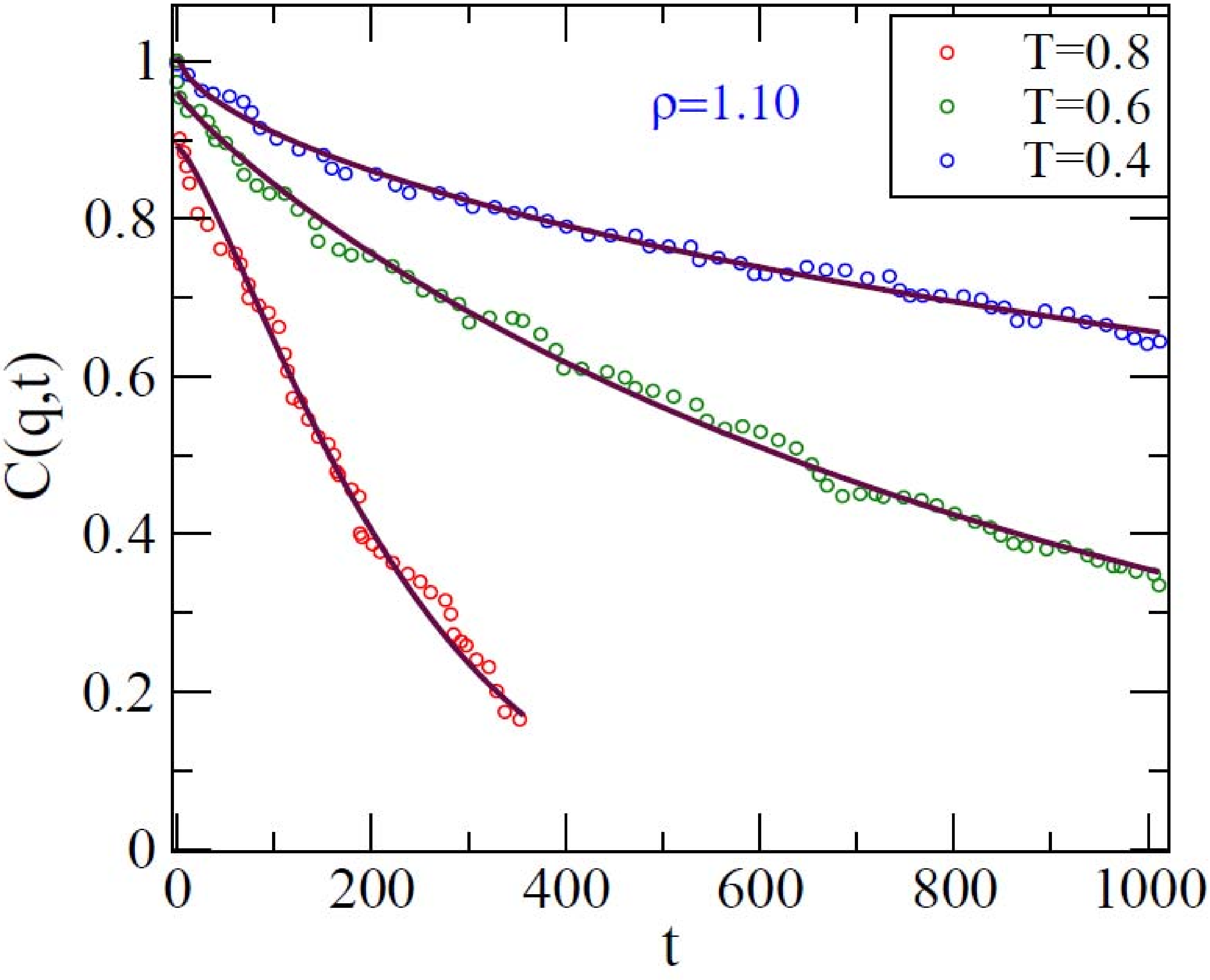


Time is in Lennard-Jones units

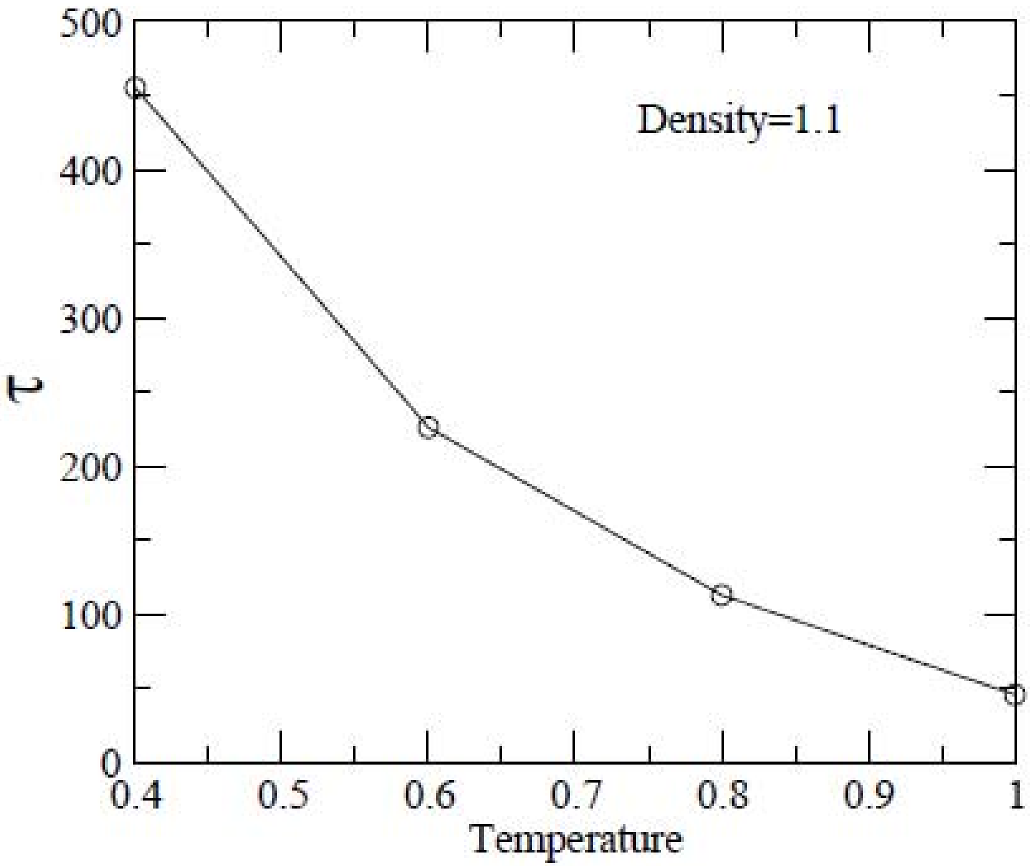


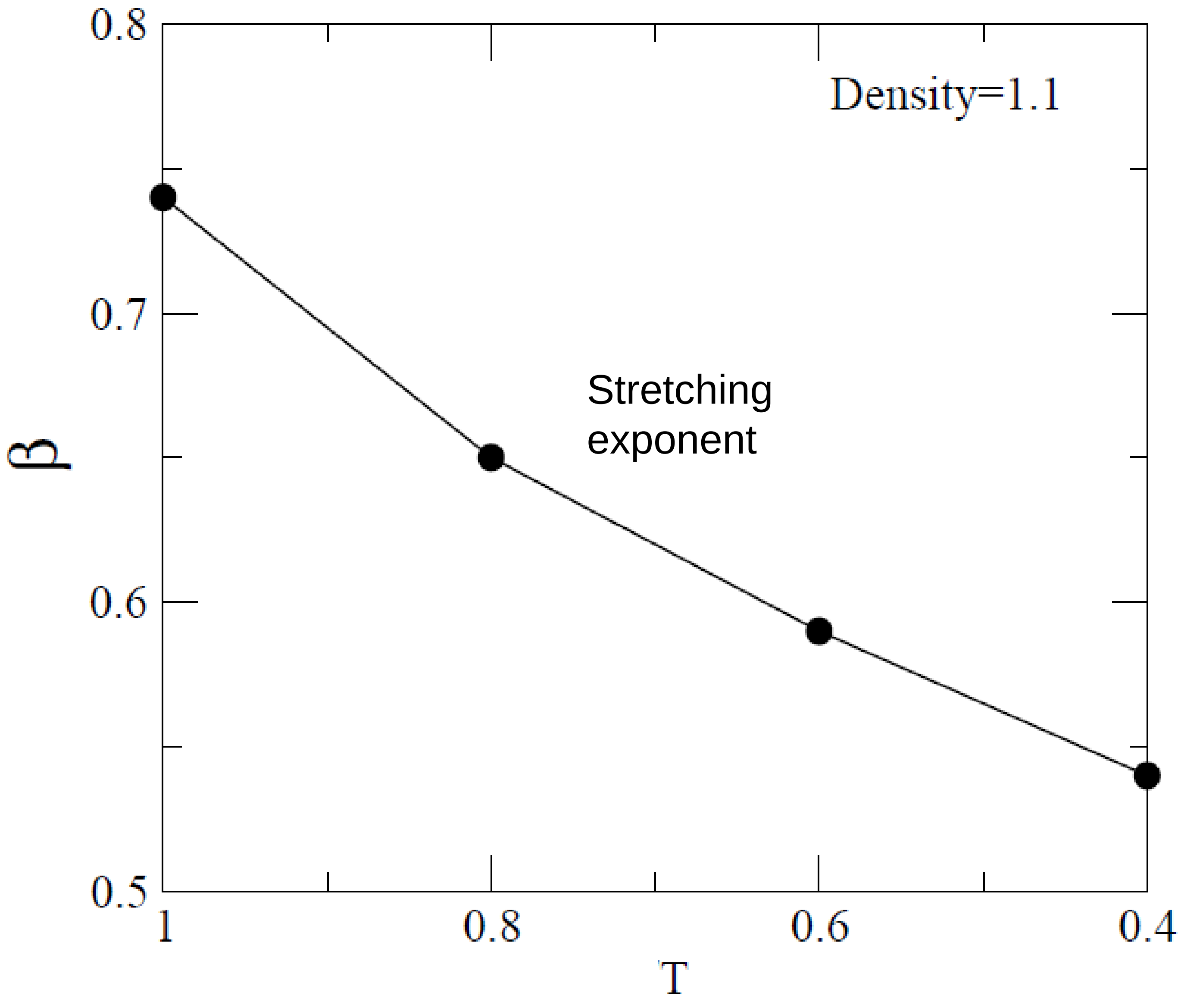
$\rho_0\sigma^3 = 1.10$
T=0.6
C(q,t)
t
S(q)
q
0
0.2
0.4
0.6
0.8
1
200
400
600
800
1000
5
6
7
8
9
2
4

Two point correlation function



The relaxation time changes by a few orders of magnitude as the tempearture is lowered at a constant density in the Lennard-Jones system




0.8
0.7
0.6
0.5
β
Density=1.1
Stretching
exponent
1
0.8
0.6
0.4
T

The four point correlation function

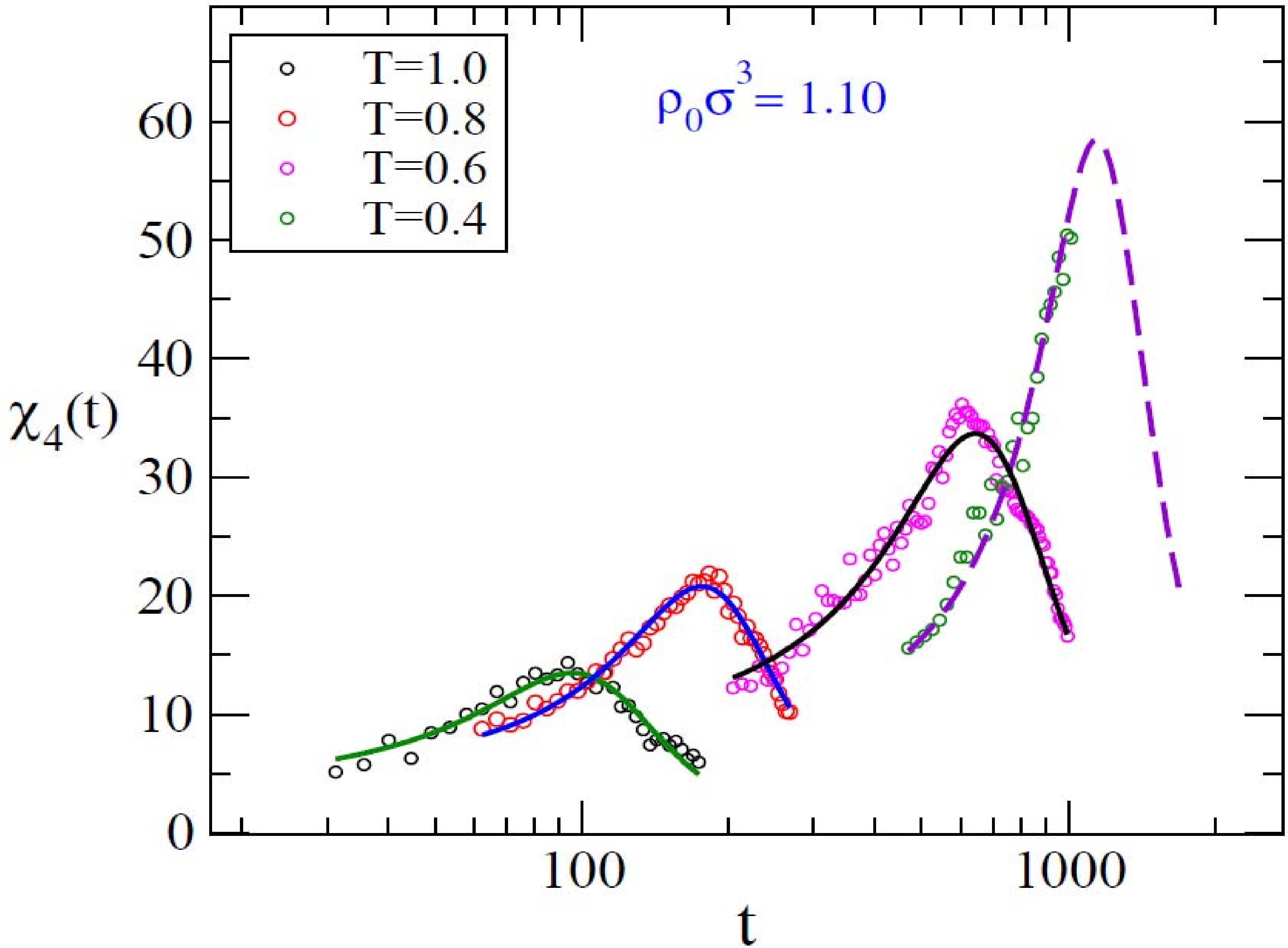
$$\lim_{t\to\infty} < \delta\rho(\mathbf{x},t)\delta\rho(\mathbf{x},0) >= \lim_{t\to\infty} < \psi(\mathbf{x},t) >= 0$$

Order paramter of the MCT.

$$\begin{aligned}\mathcal{G}_4(\mathbf{x},t) &= < \delta\rho(\mathbf{0},t)\delta\rho(\mathbf{0},0)\delta\rho(\mathbf{x},t)\delta\rho(\mathbf{x},0) > \\ &- < \delta\rho(\mathbf{0},t)\delta\rho(\mathbf{0},0) >< \delta\rho(\mathbf{x},t)\delta\rho(\mathbf{x},0) > \\ &= < \psi(\mathbf{0},t)\psi(\mathbf{r},t) > - < \psi(\mathbf{0},t) >< \psi(\mathbf{r},t) >\end{aligned}$$

$$\phi(t) = \frac{1}{V}\int d\mathbf{x}\psi(\mathbf{x},t)$$

$$V\left[< \phi^2(t) > - < \phi(t) >^2\right]$$



T=1.0
T=0.8
T=0.6
T=0.4
$\rho_0\sigma^3 = 1.10$
$\chi_4(t)$
0
10
20
30
40
50
60
100
1000
t

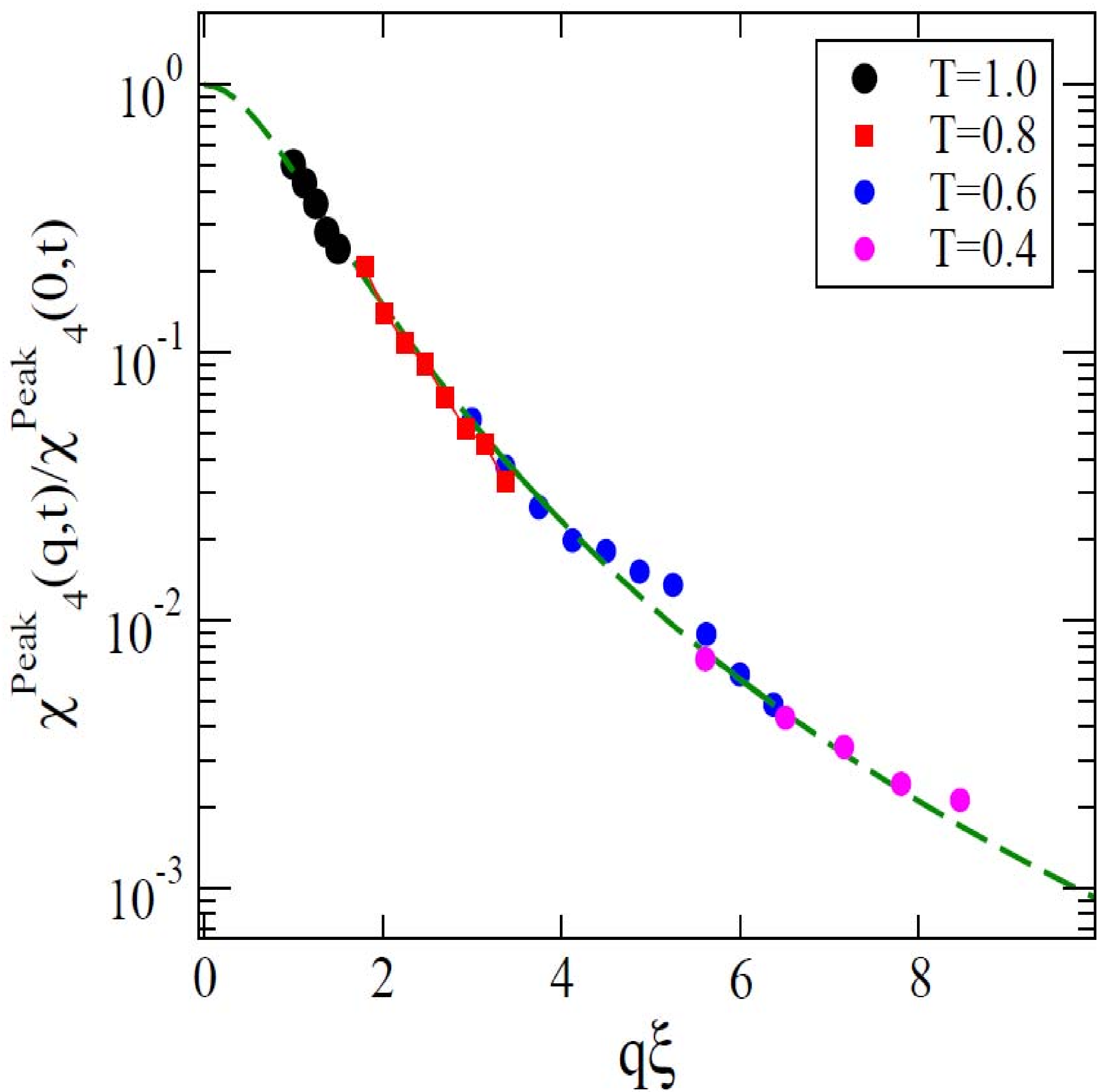
Nongaussian behavior

Four point function with collective density fluctuations : Measure of the departure from Gaussian approximation.

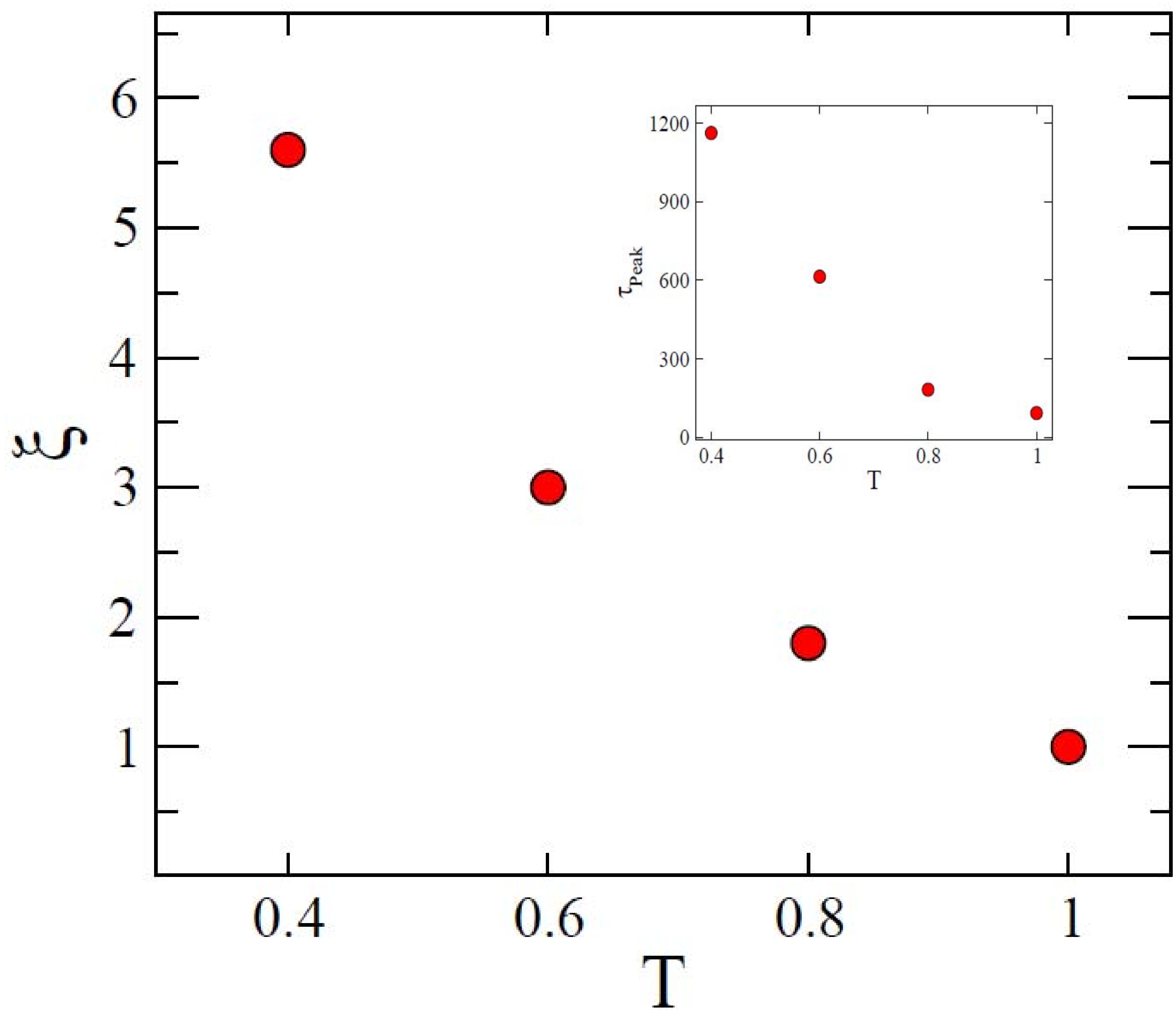
Four point correlation ⟶

Product of two point correlation

(Beyond one loop approximation in the MSR field theoretic model)



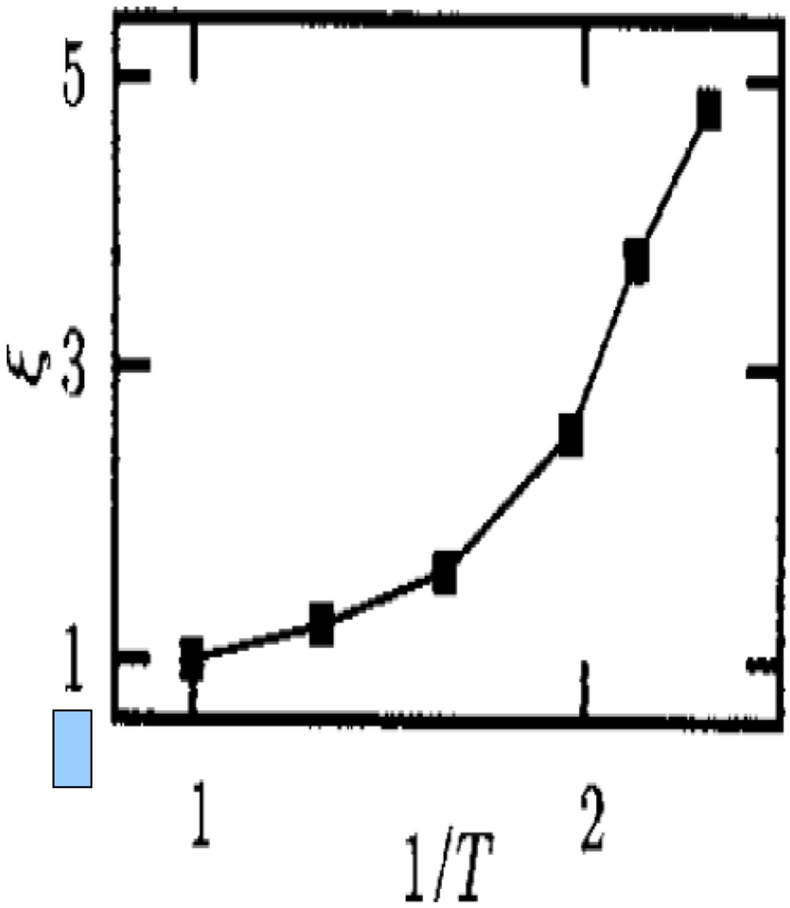
T=1.0
T=0.8
T=0.6
T=0.4
$\chi_4^{Peak}(q,t)/\chi_4^{Peak}(0,t)$
10^0
10^{-1}
10^{-2}
10^{-3}
0
2
4
6
8
qξ



6
5
4
3
2
1
ξ
0.4
0.6
0.8
1
T
1200
900
600
300
0
τPeak
0.4
0.6
0.8
1
T

Molecular dynamics

(Berthier et. al. 2007)



Summary

- Dynamic length scale identified from four point Correlation functions.
- Solution of FNH equations. Negative density instability removed with coarse graining
- Equations with the $1/\rho$ nonlinearities in the dynamics
- Growing dynamic correlation length