Flow Properties of Complex Fluids

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Complex Fluids:

- colloidal dispersions
- polymeric liquids
- anisotropic fluids
  - liquid crystals
  - ferro-fluids
  - magneto- and electro-rheological fluids

Methods:

- Irreversible Thermodynamics
- Kinetic Theory
- Non-Equilibrium Molecular Dynamics: NEMD

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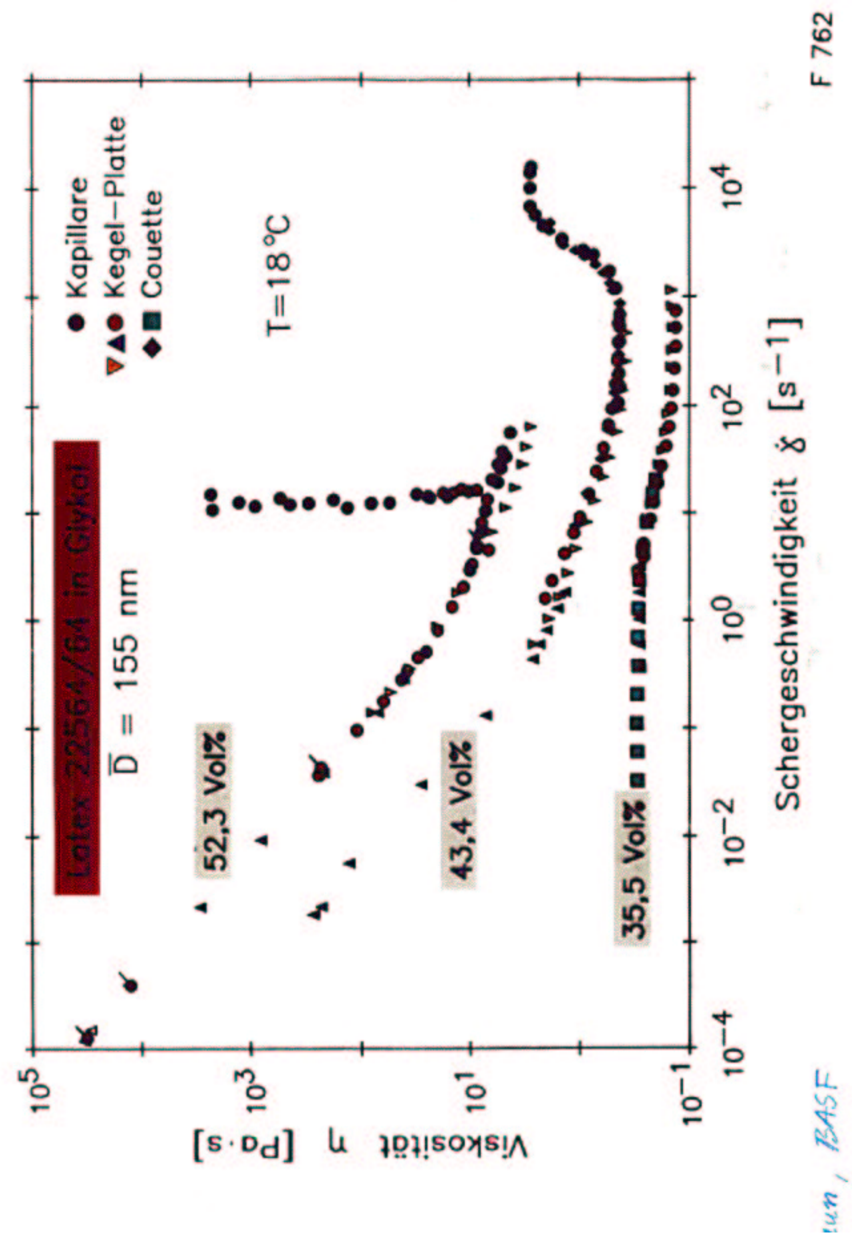
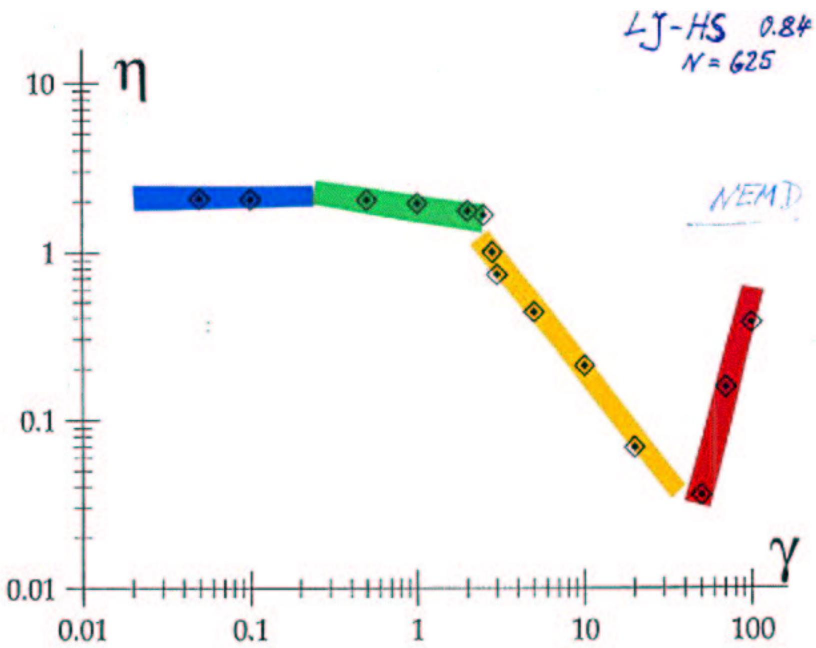
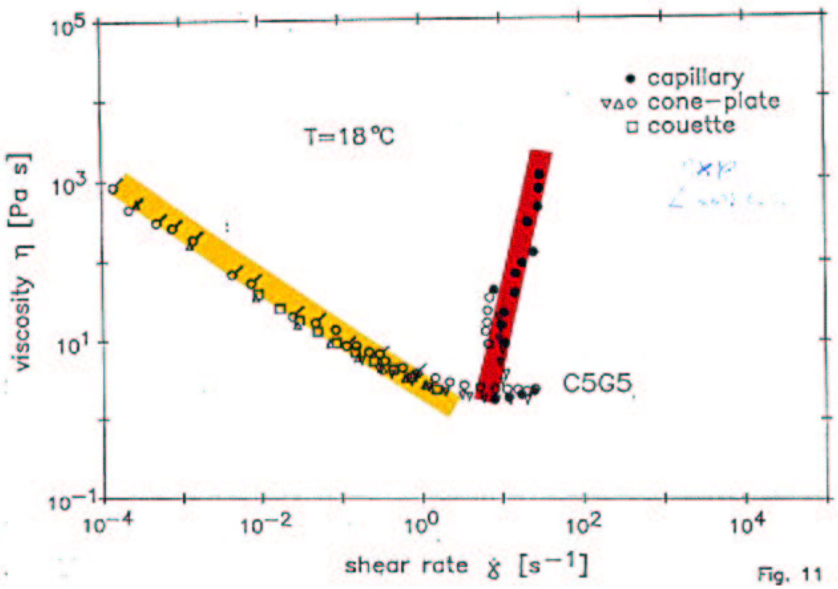






S.Hess

2 MD and NEMD Computer-Simulations

2.1 N-particle dynamics

The classical equations of motion

$$m\frac{d^2}{dt^2}\mathbf{r}_i = \mathbf{F}_i = \Sigma_{i\neq j}\mathbf{F}_{ij}$$

of N particles with mass m at positions $\mathbf{r}_i$ feeling the forces $\mathbf{F}_i$ are integrated numerically,
in general, subject to certain constraints.
The pair force $\mathbf{F}_{ij} = \mathbf{F}$ can be derived from the pair potential Φ :

$$\mathbf{F}(\mathbf{r}) = -\nabla\Phi(\mathbf{r})$$

where $\mathbf{r} = \mathbf{r}_{ij}$ is the relative position vector.

2.2 Averages

Macroscopic quantities like

- internal energy
- pressure (tensor)
- velocity distribution function
- pair correlation function
- static and dynamic structure factor

are evaluated according to the rules of *Statistical Physics* from the positions and velocities of N particles and averaged over many time steps.

2.3 Potentials

Lennard-Jones Potential (LJ)

$$\phi^{LJ}(\mathbf{r}) = 4\varepsilon_{LJ}\left(\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right)$$

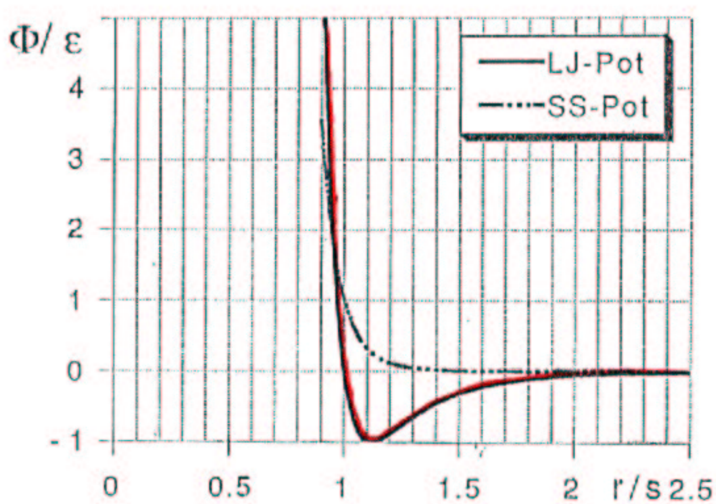
almost *Hard Spheres*(HS)
repulsive part of LJ-pot. (cut off at $r = 1.12 r_0$)

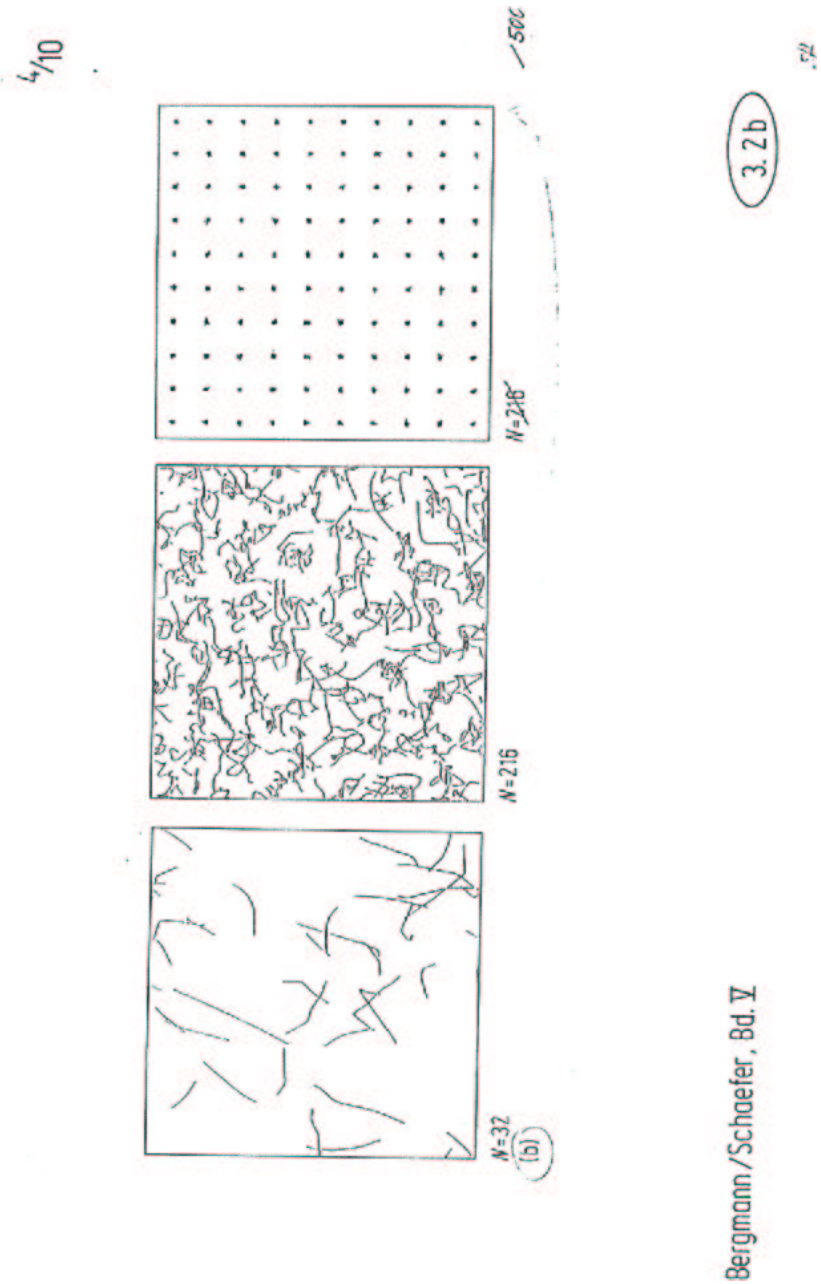
Soft-Spheres (SS)

$$\phi^{SS}(\mathbf{r}) = \varepsilon_{SS}\left(\frac{r_0}{r}\right)^{12}$$

SS + screened repulsive Coulomb-pot. (Disp)

$$\phi^{Disp}(\mathbf{r}) = \varepsilon_{SS}\left(\frac{r_0}{r}\right)^{12} + B\frac{r_0}{r}e^{-r \cdot}$$





2.4 Scaling

With the help of the reference values r_0, ϵ, m for the length, energy and mass, all physical quantities A are associated with dimensionless variables A^* according to:

$$A = A^* A_{ref}.$$

reference values

density.................. $n_{ref} = r_0^{-3}$

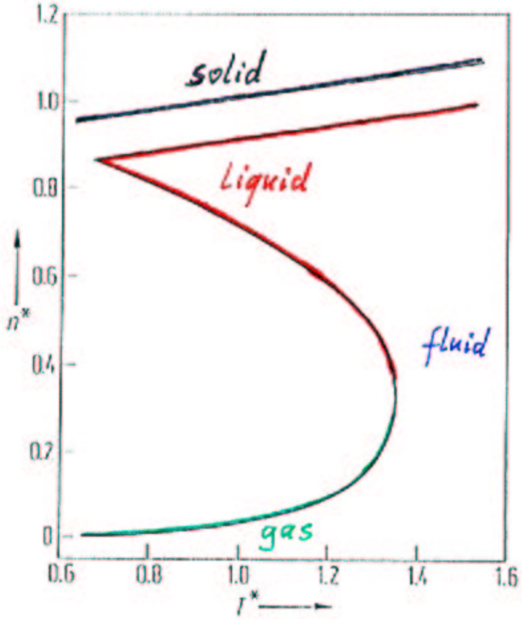
temperature ...... $k_B T_{ref} = \epsilon$

pressure .... $p_{ref} = r_0^{-3}\epsilon$

time .. .. $t_{ref} = r_0 \epsilon^{-1/2} m^{1/2}$

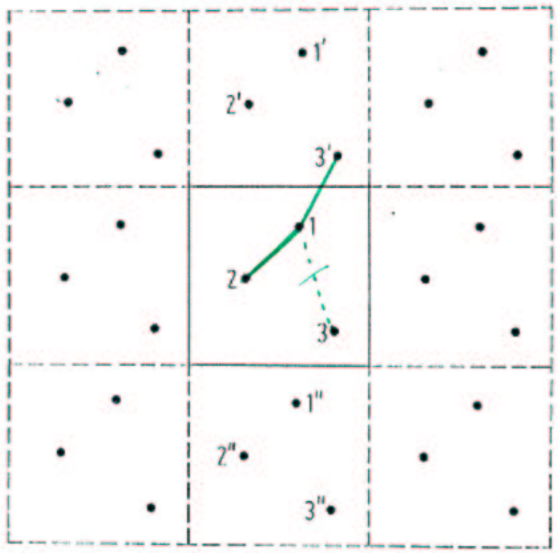
shear rate............ $\gamma_{ref} = t_{ref}^{-1}$

viscosity.......... $\eta_{ref} = r_0^{-2}\epsilon^{1/2} m^{1/2}$



2.5 Periodic Boundary Conditions

The volume V of the basic cell (box) is inferred from the number N of particles and the number density $n = N/V$.
For a cubic box the cell length L is given by $L = V^{-1/3}$.
The range of the forces is less than $L/2$.



2.6 Temperature Control

$T = const$

$$3k_B T = N^{-1} m \sum_i \mathbf{c}_i^2$$

$$\mathbf{c}_i = \dot{\mathbf{r}}_i - \mathbf{v}(\mathbf{r}_i)$$

v flow velocity
$\mathbf{c}_i$ peculiar velocity

2.7 MD and NEMD

NEMD

Non-Equilibrium-Molecular-Dynamics Computer-Simulation

relaxation phenomena

stationary transport processes

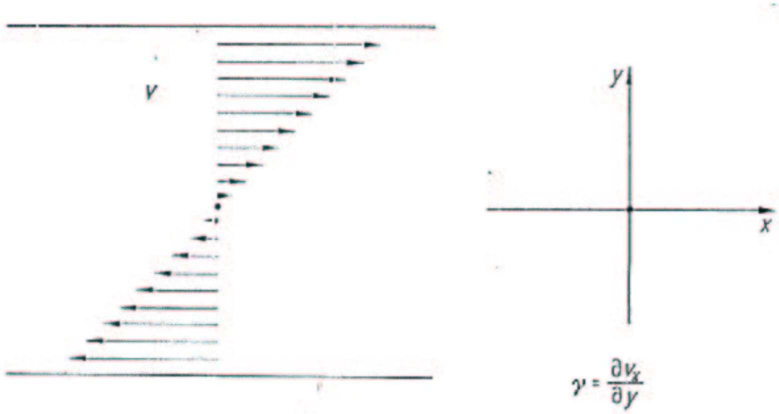
e.g. simulation of a plane *Couette*-flow

2.8 plane Couette flow

$$\mathbf{v}_x = \gamma y, \quad \mathbf{v}_y = 0, \quad \mathbf{v}_z = 0$$

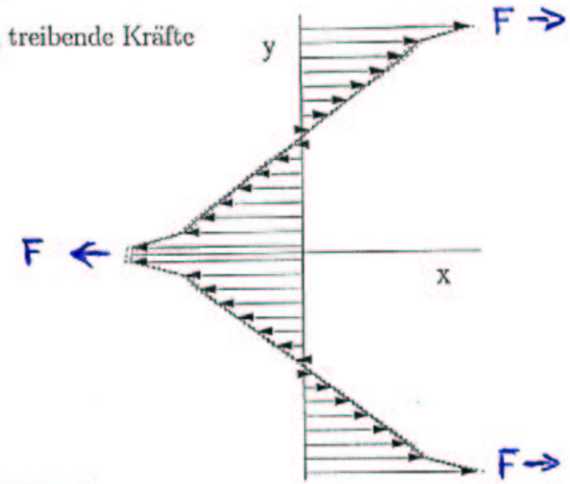
shear rate

$$\gamma = \frac{\partial \mathbf{v}_x}{\partial y}.$$

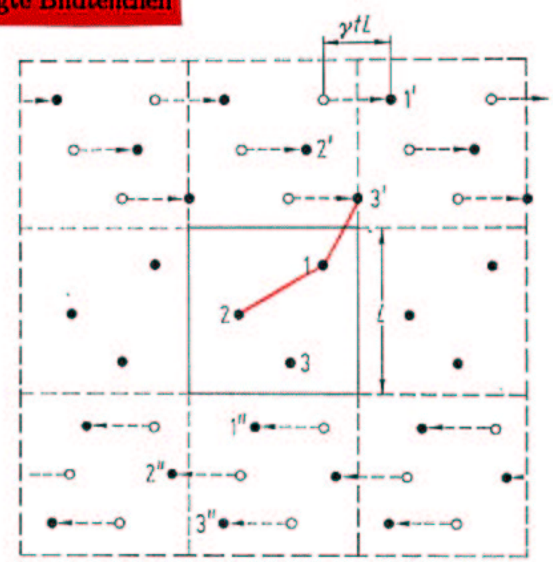


2.2 Simulation

bewegte Wände, treibende Kräfte



bewegte Bildteilchen



2.10 Rheological Behavior, Pressure Tensor

$$\mathbf{p} = \mathbf{p}^{kin} + \mathbf{p}^{pot},$$

kinetic contribution

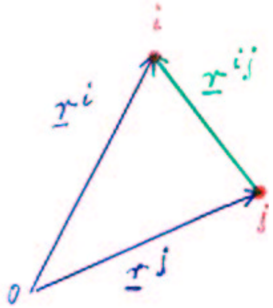
$$\mathbf{p}^{kin}_{xy} = V^{-1} m \sum_i \mathbf{c}^i_x \mathbf{c}^i_y.$$

$$\mathbf{c}^i = \dot{\mathbf{r}}^i - \mathbf{v}(\mathbf{r}^i)$$

potential contribution

$$\mathbf{p}^{pot}_{xy} = V^{-1} \frac{1}{2} \Sigma \Sigma_{i \neq j} \mathbf{r}^{ij}_x \mathbf{F}^{ij}_y.$$

$$\mathbf{r}^{ij} = \mathbf{r}^i - \mathbf{r}^j$$



$$\mathbf{p}^{kin} = m \int \mathbf{c}\mathbf{c} f(\mathbf{c})\, d^3c$$

$$\mathbf{p}^{pot} = \frac{1}{2} n^2 \int \mathbf{r}\mathbf{F} g(\mathbf{r})\, d^3r$$

particle density $n = N/V$

shear modulus

$$G = V^{-1} \frac{1}{30} \Sigma \Sigma_{i \neq j} r_{ij}^{-2} \left(r_{ij}^4 \phi'_{ij} \right)'$$

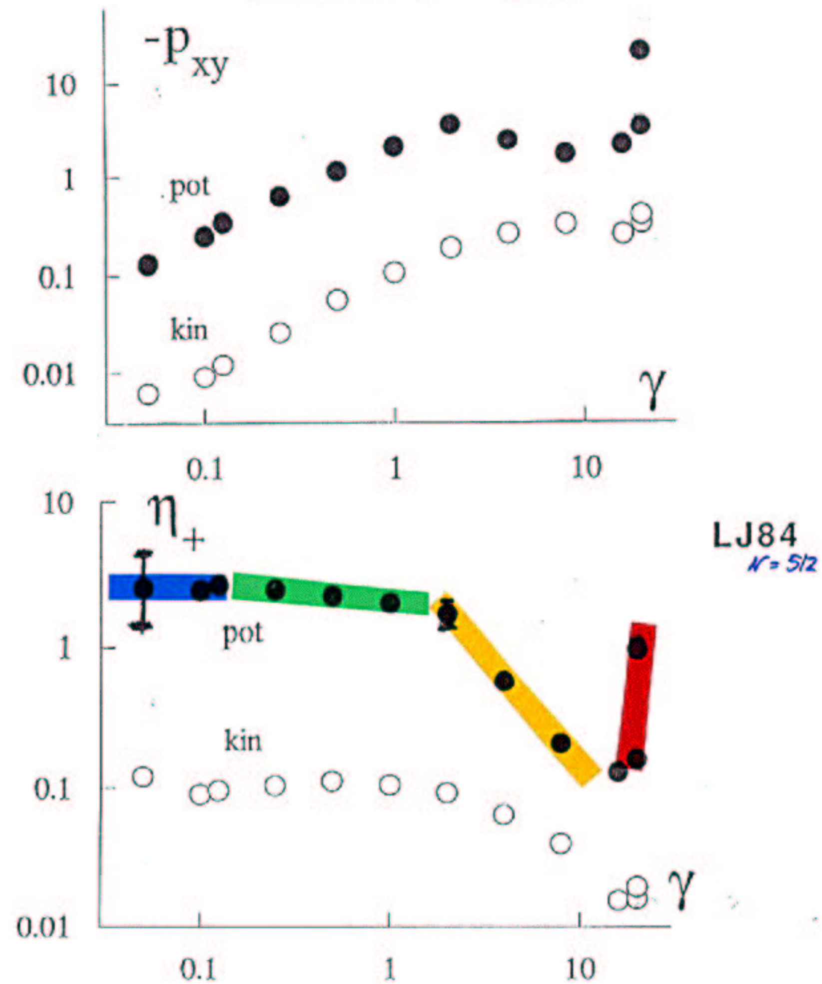
$$r_{ij} = \|\mathbf{r}_{ij}\| \text{and} \phi_{ij} = \phi(\mathbf{r}_{ij})$$

12

3.2 Viscosität dichter Fluide

Ergebnisse für LJ, LJ-HS, SS, Disp

$$Viscosität\ \eta = -p_{xy}/\gamma$$



9

4 The Structure of Streaming Fluids

4.1 Expansion of the Pair-Correlation Function for a Plane Couette Flow

$$g(\mathbf{r}) = g_S(r) + g_+(r)\hat{x}\hat{y} + g_-(r)\frac{1}{2}\left(\hat{x}^2 - \hat{y}^2\right) + g_0(r)\left(\hat{z}^2 - \frac{1}{3}\right) + \dots, \quad (47)$$

$\hat{x}$, $\hat{y}$, $\hat{z}$ are the Cartesian components of $\hat{\mathbf{r}}$.

$\ell = 0$

$$g_S = (4\pi)^{-1} \int g(\mathbf{r})\, d^2\hat{r}. \quad (48)$$

$\ell = 2, 4, \dots$

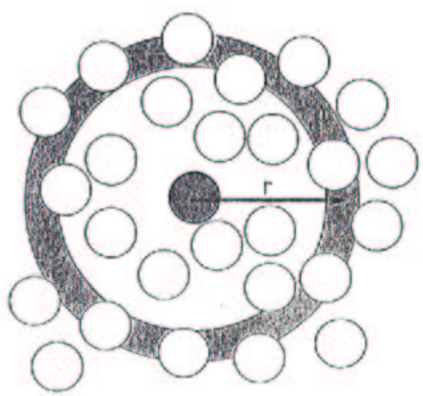
$$g_k = (4\pi)^{-1} \int Y_k(\hat{\mathbf{r}})\, g(\mathbf{r})\, d^2\hat{r} \quad (49)$$

$$Y_+ = 2\hat{x}\hat{y}, \qquad Y_- = \hat{x}^2 - \hat{y}^2, \qquad Y_0 = \frac{3}{2}\left(\hat{z}^2 - \frac{1}{3}\right). \quad (50)$$

$$K_4 = \frac{5}{4}\sqrt{21}\left(\hat{x}^4 + \hat{y}^4 + \hat{z}^4 - \frac{3}{5}\right); \quad (51)$$

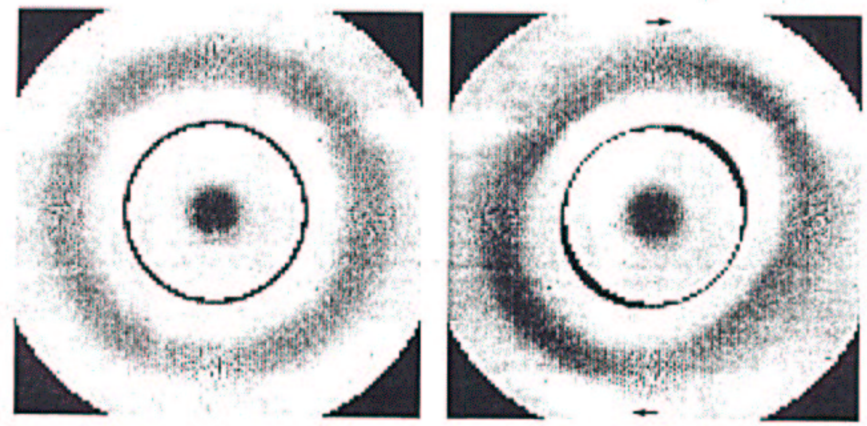
$$p_k = -\frac{2\pi}{15} n^2 \int_0^\infty r\phi'\, g_k(r)\, r^2\, dr, \qquad k = +, -, 0 \quad (52)$$

$$p - p_{eq} = -\frac{2\pi}{3} n^2 \int_0^\infty r\, \phi'\, (g_S(r) - g_{eq})\, r^2\, dr. \quad (53)$$



Pair-correlation function g(r)

15



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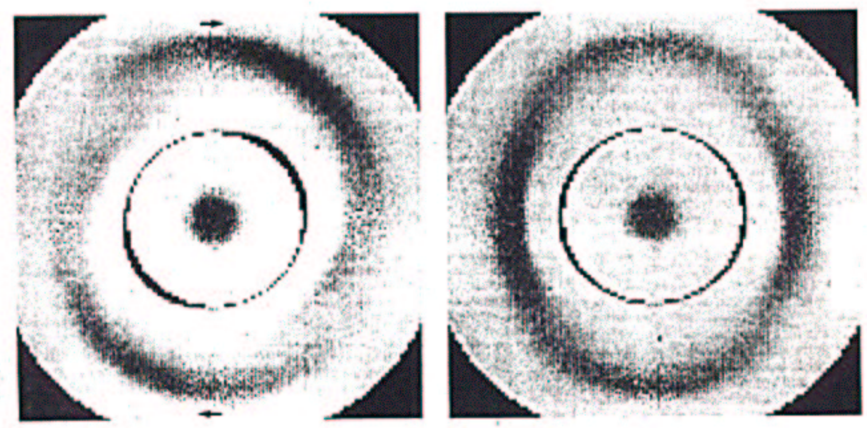

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3.8 Gereralized Stokes–Maxwell Model

The structural changes in the flow regimes I and II can be treated by starting from a Kirkwood–Smoluchowki type of kinetic equation for the pair correlation function $g = g(\mathbf{r})$:

$$\partial g/\partial t + \Gamma\, r_y\, \partial g/\partial r_x + \mathcal{D}(g) = 0\,. \qquad (43)$$

"damping" term $\mathcal{D}(g)$ ensures that g approches the equilibrium pair correlation function g_{eq}

$$\mathcal{D}(g) = \tau^{-1}\,(g - g_{eq})\,, \qquad (44)$$

τ Maxwell relaxation time

stationary situation,

$$g = g_{eq} - \Gamma\tau\, r_y\, \partial g/\partial r_x\,. \qquad (45)$$

$$g = g_{eq} - \Gamma\tau\, r_x\, r_y\, r^{-1} g'_{eq} + (\Gamma\tau)^2\, \left(r_y^2 r^{-1} g'_{eq} + r_x^2 r_y^2 r^{-1}(r^{-1} g'_{eq})'\right) - .. + \ldots \qquad (46)$$

linear Stokes–Maxwell relation:

$$g_+ = g_{45} - g_{135} = -\Gamma\tau\, r g'_{eq}$$

test for a Lennard-Jones liquid

Stokes–Maxwell:

$$p_{yx}^{pot} = -\eta^{pot}\,\Gamma$$
$$\eta^{pot} = G\,\tau \qquad (47)$$

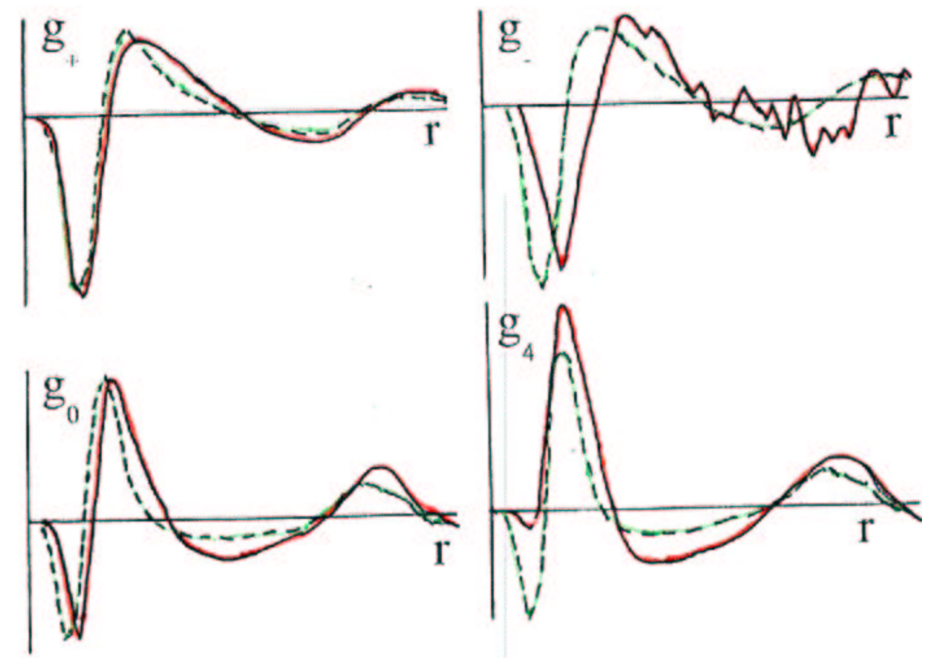
. (high frequency) shear modulus G

$$G = -\frac{1}{2} n^2 \int y\partial\Phi/\partial x\, y\partial g_{eq}/\partial x\, d^3r = \frac{1}{2} n^2 \int y^2 \partial^2\Phi/\partial x^2\, g_{eq}\, d^3r\,, \qquad (48)$$

spherical interaction and a system in an isotropic state: Born–Green expression

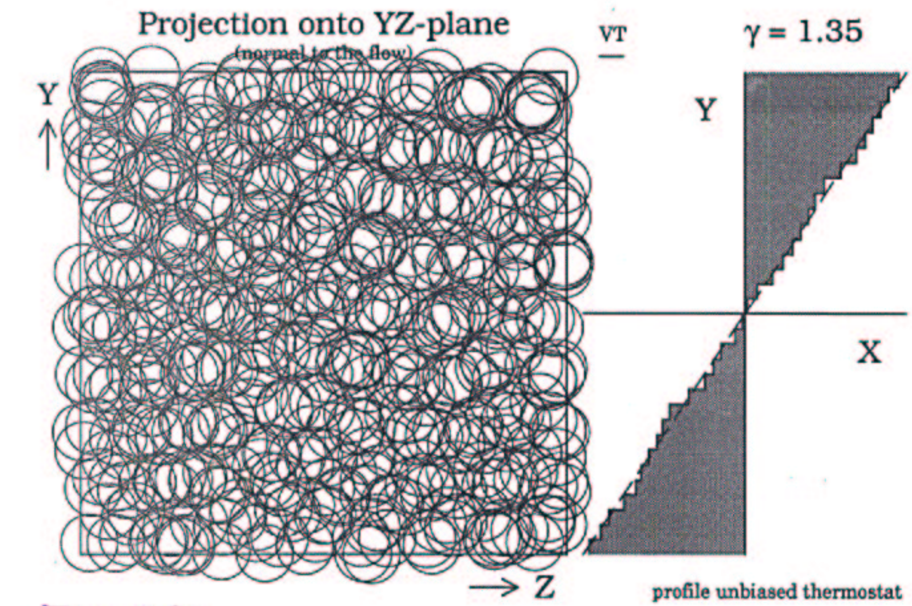
$$G = (1/30) \int r^{-2}(r^{-1}\Phi')'\, d^3r$$

14

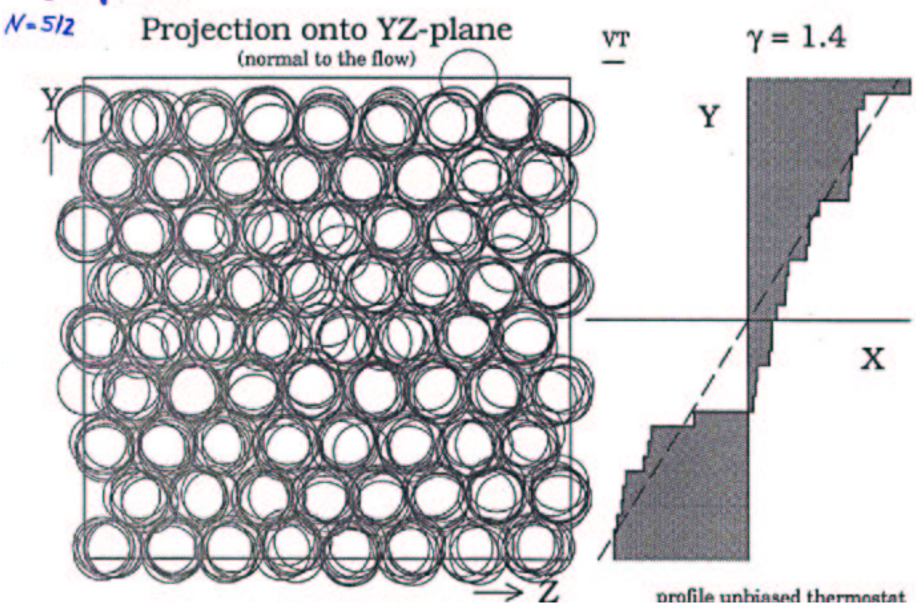


SS $n = 0.7$ $T = 0.25$

$\dot\gamma = 1$

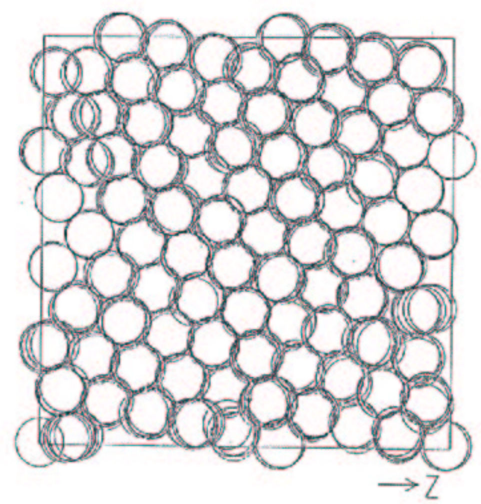


Disp 0.84
N=512

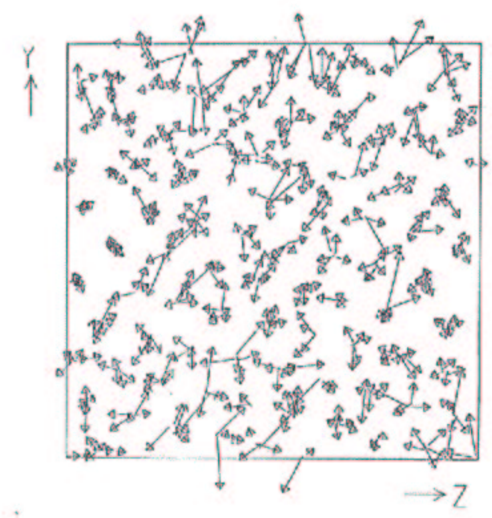


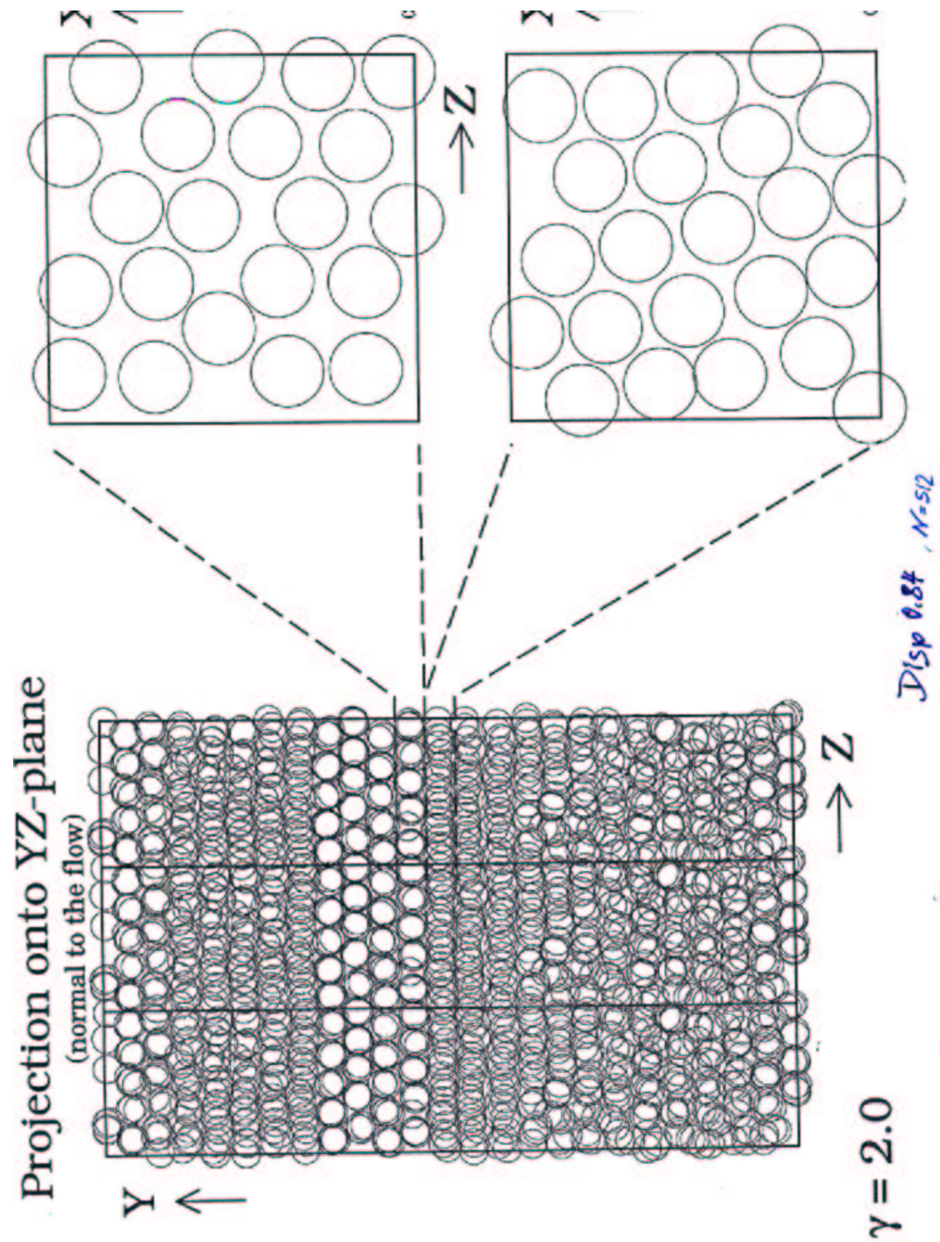
4.2 scherinduzierte Positionsordnung

Schnappschuss-Aufnahmen
Geschwindigkeitsprofile



LJ 0.84
N = 512





4.3 Licht- und Neutronen-Streuung

statischer ***Strukturfaktor***

$$S(\mathbf{k}) = 1 + n \int e^{i\mathbf{k}\cdot\mathbf{r}} \left(g(\mathbf{r}) - 1\right)\ d^3r.$$

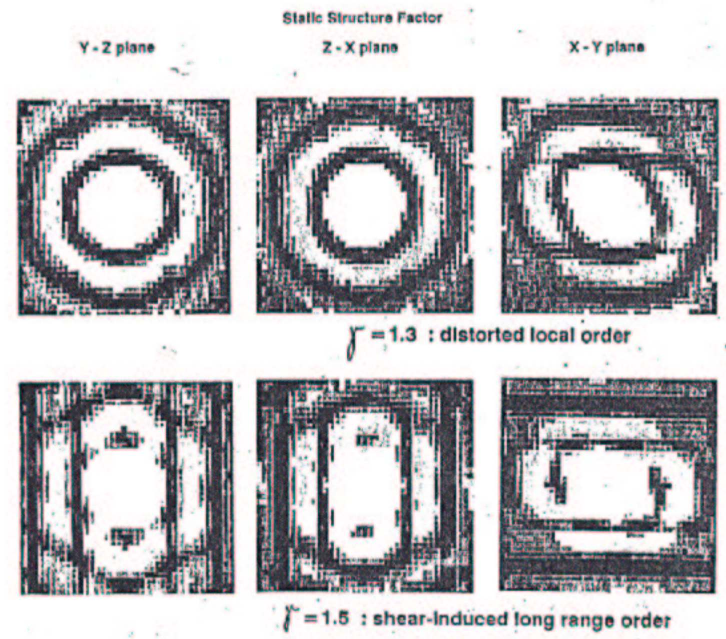
$$S(\mathbf{k}) = N^{-1}\left(\left(\sum_j \cos \mathbf{k}\cdot\mathbf{r}^j\right)^2 + \left(\sum_j \sin \mathbf{k}\cdot\mathbf{r}^j\right)^2\right).$$

$$S(\mathbf{k}) = 1 + N^{-1}\sum\sum_{i\neq j} \cos \mathbf{k}\cdot\mathbf{r}^{ij}$$

Intensität

$$I = PS$$

Formfaktor P



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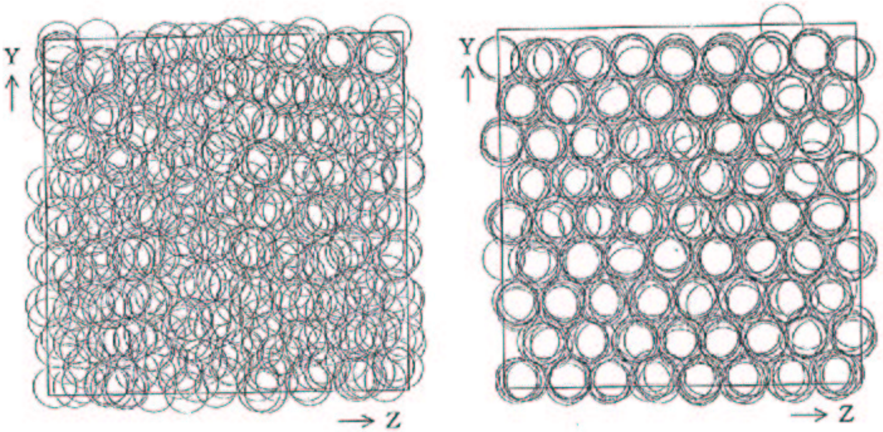
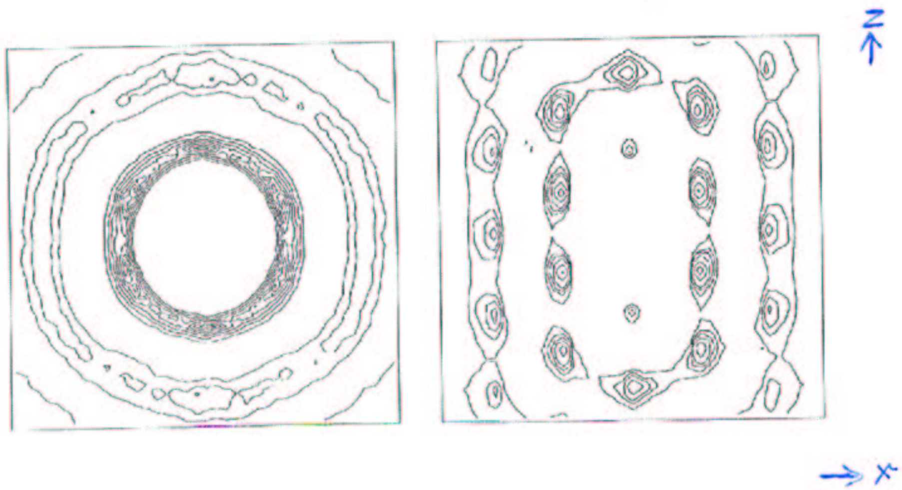
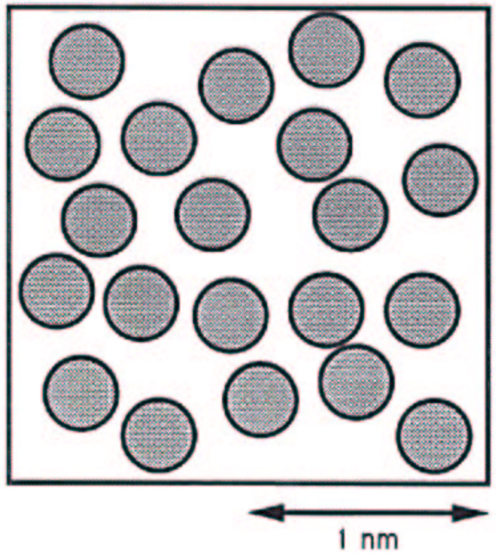


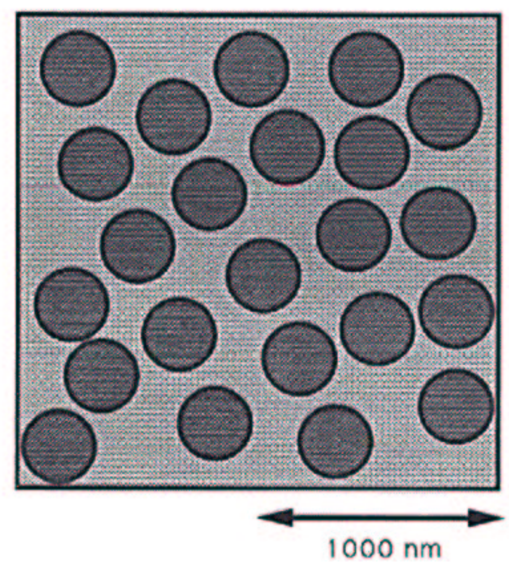
Disp 9.84 , N = 512





atomic fluid

colloidal dispersion



Rheological and small angle neutron scattering investigation of shear-induced particle structures of concentrated polymer dispersions submitted to plane Poiseuille and Couette flow[a]

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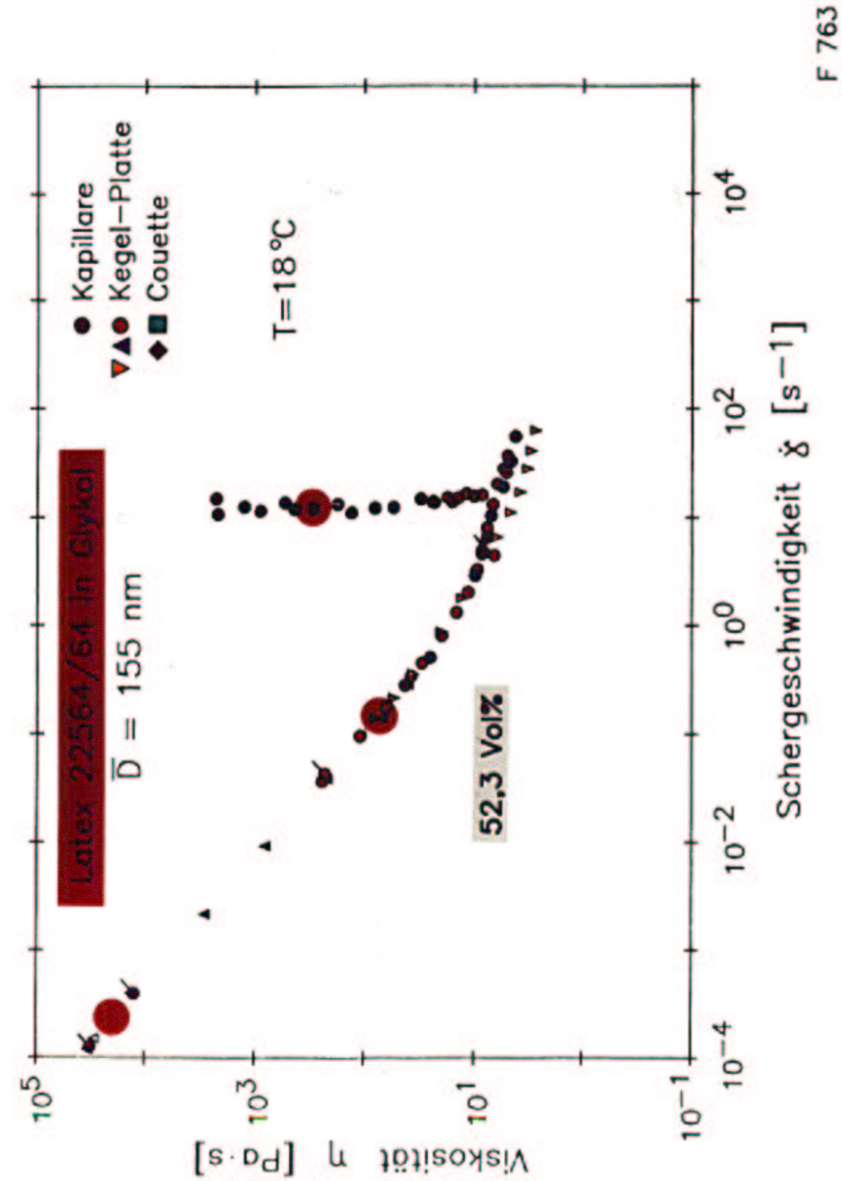
(Received 3 June 1991; accepted 24 February 1992)

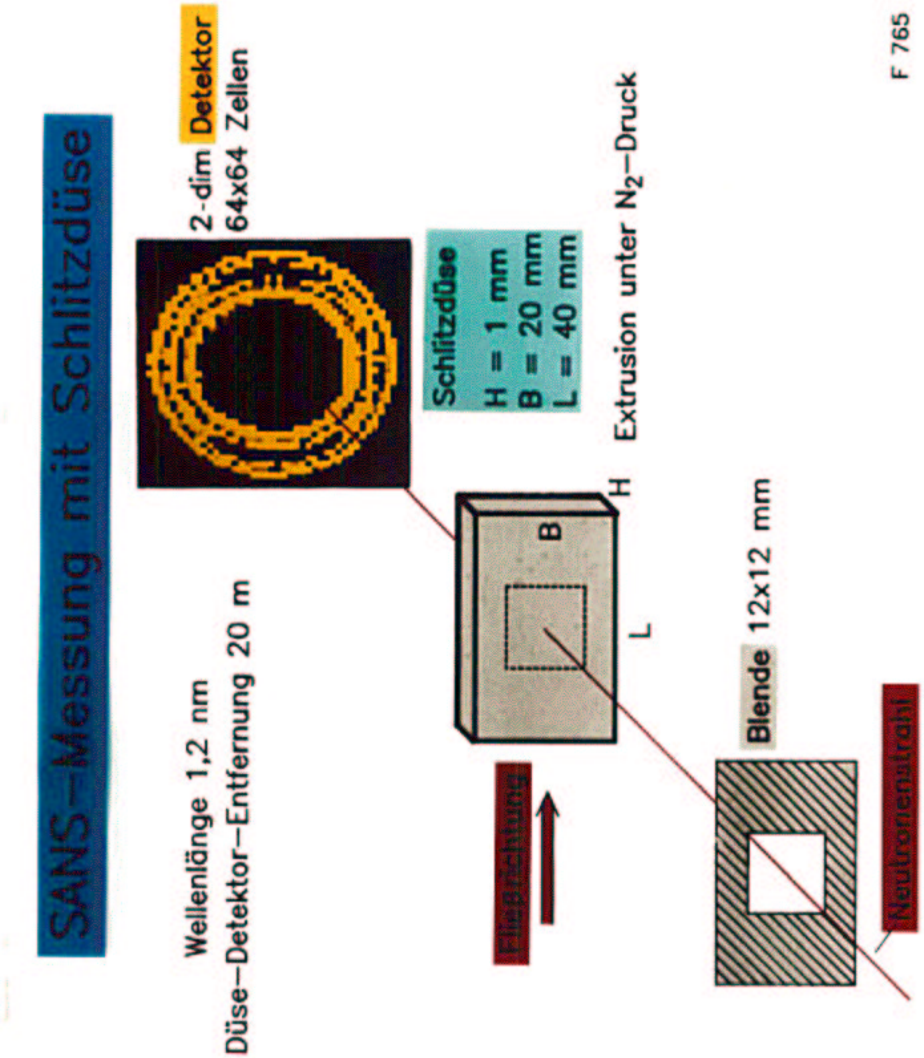
Synopsis

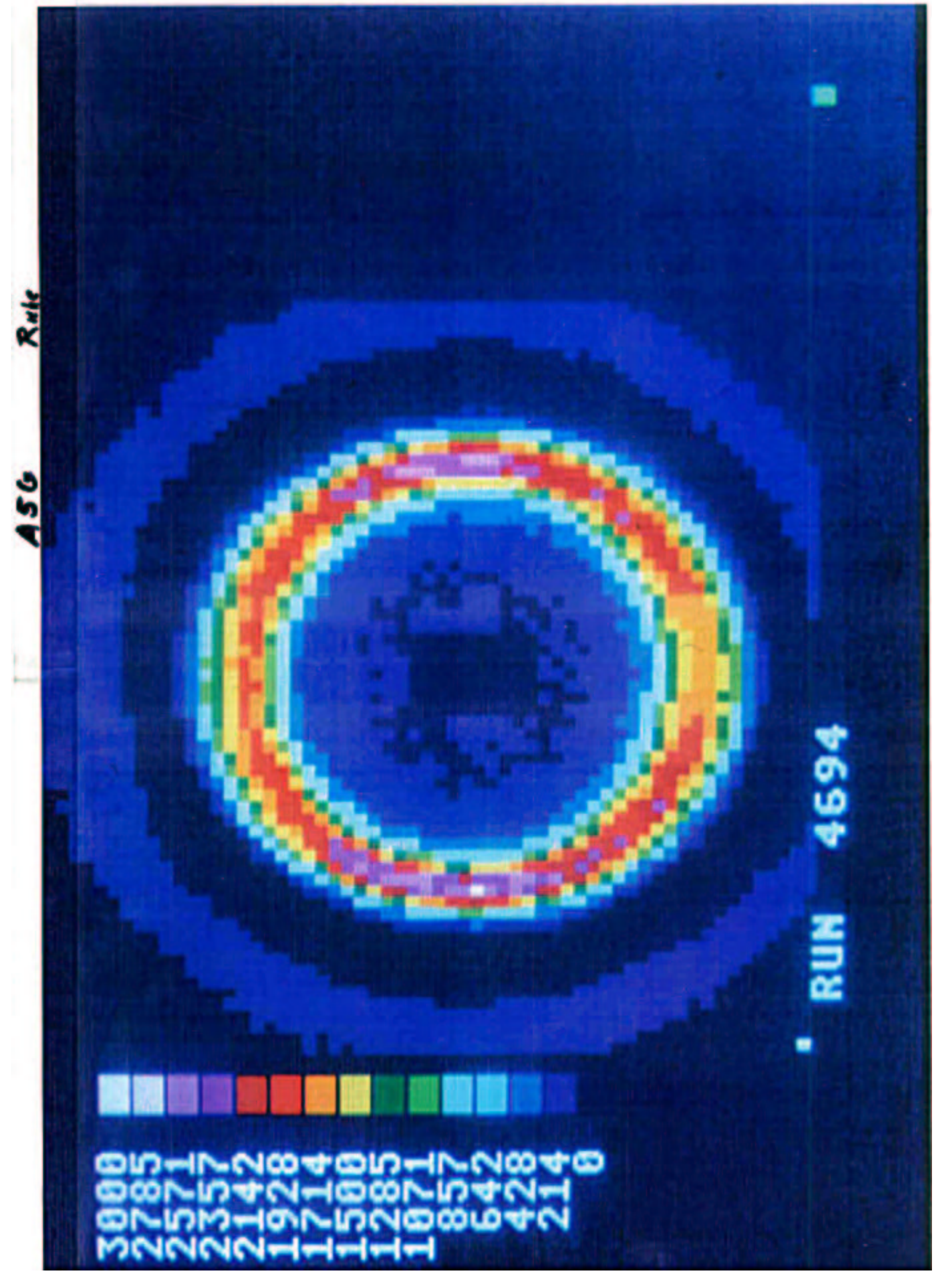
Shear-induced particle structures of rheologically well-characterized concentrated polymer dispersions were investigated by small angle neutron scattering (SANS) in a wide range of shear rates. The dispersions consist of electrostatically stabilized styrene–ethylacrylate–copolymer spheres in glycol or water. Their viscosity functions show pronounced shear thinning and strong shear thickening versus shear rate as measured by various rotational rheometers and by capillary rheometry. A quartz slit die, which could be tilted with regard to the neutron beam, enabled us to achieve wall shear rates as low as $10^{-5}\,s^{-1}$ and wall shear stresses up to 10^4 Pa. Part of the measurements were repeated using a Couette shear cell. Spheres of 320 nm mean diameter at a volume concentration of 58.7% in glycol show an amorphous structure at rest. In the

[a] Dedicated to Dr. H. Willersinn on the occasion of his 65th anniversary.

J. Rheol. 36(4), May 1992 0148-6055/92/040743-45$04.00




SANS-Messung mit Schlitzdüse
2-dim Detektor
64x64 Zellen
Schlitzdüse
H = 1 mm
B = 20 mm
L = 40 mm
Extrusion unter N$_2$-Druck
F 765
H
B
L
Wellenlänge 1,2 nm
Düse-Detektor-Entfernung 20 m
Fließrichtung
Blende 12x12 mm
Neutronenstrahl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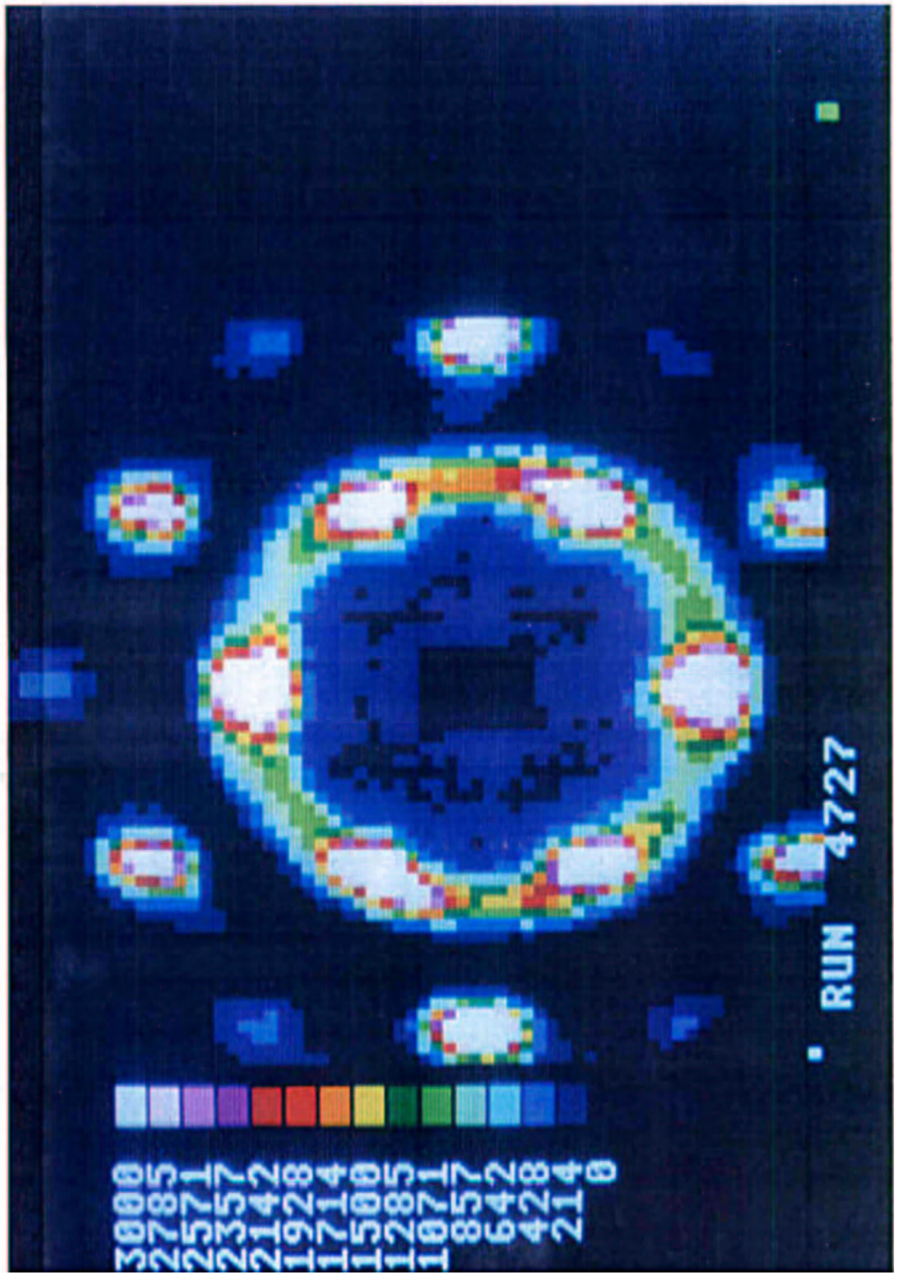
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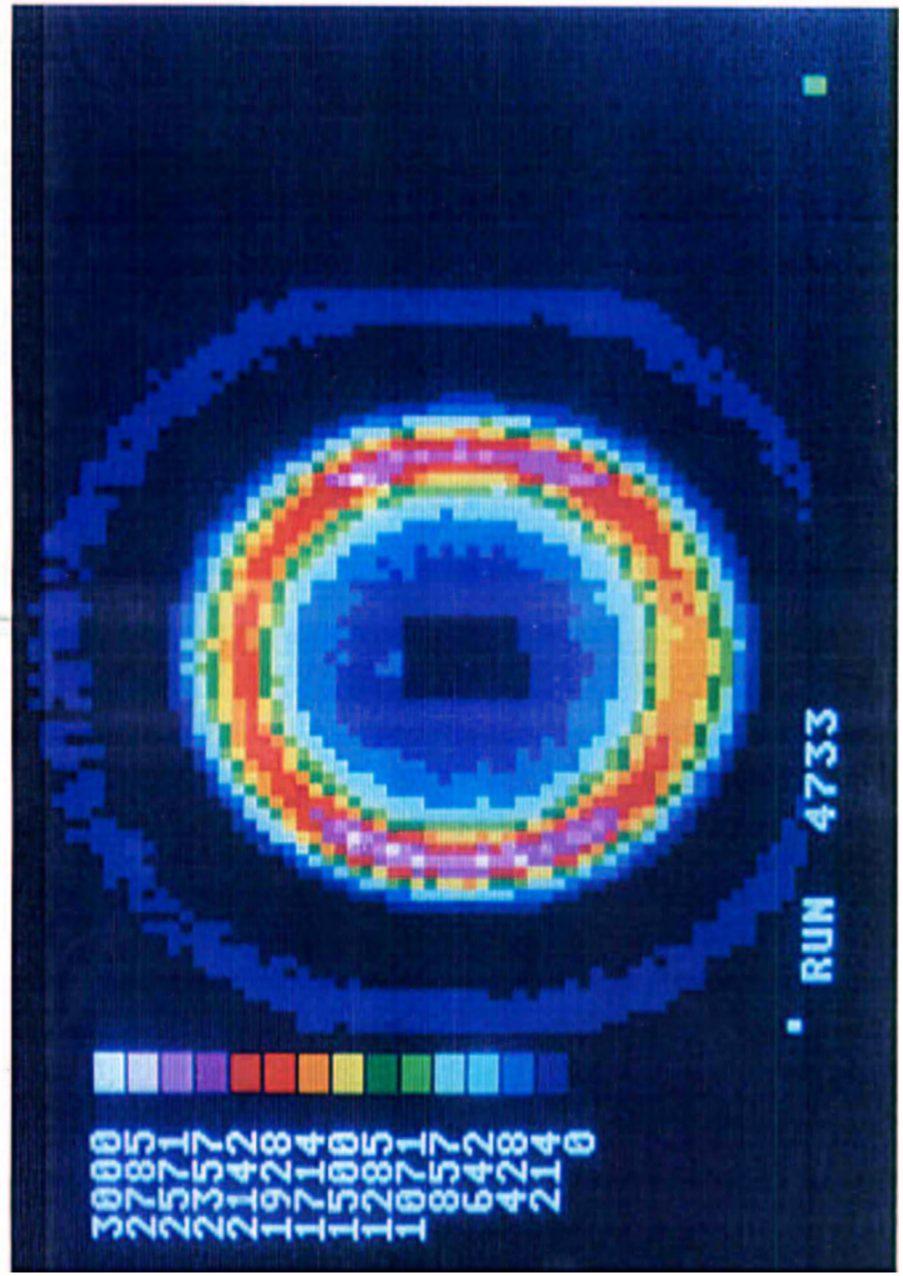
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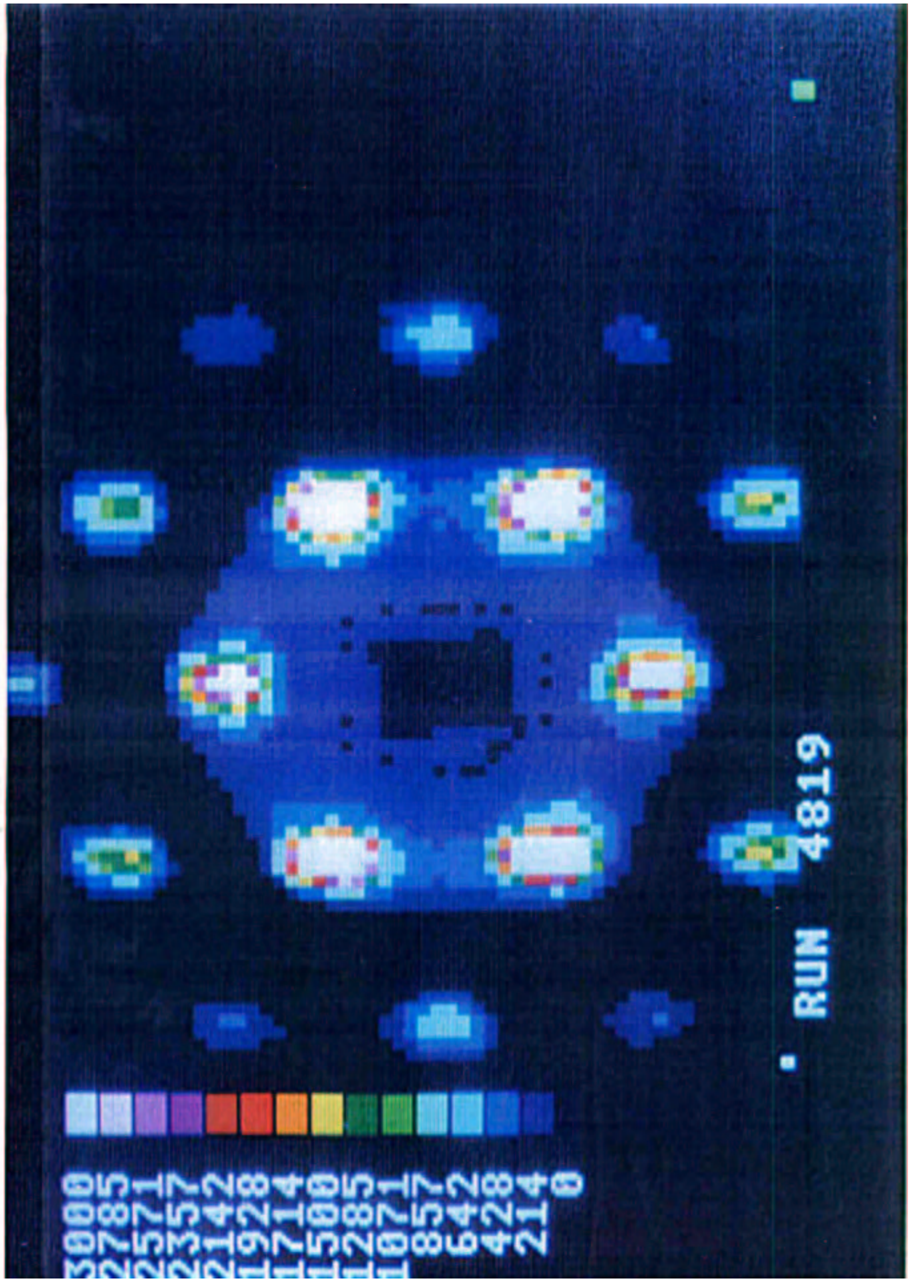
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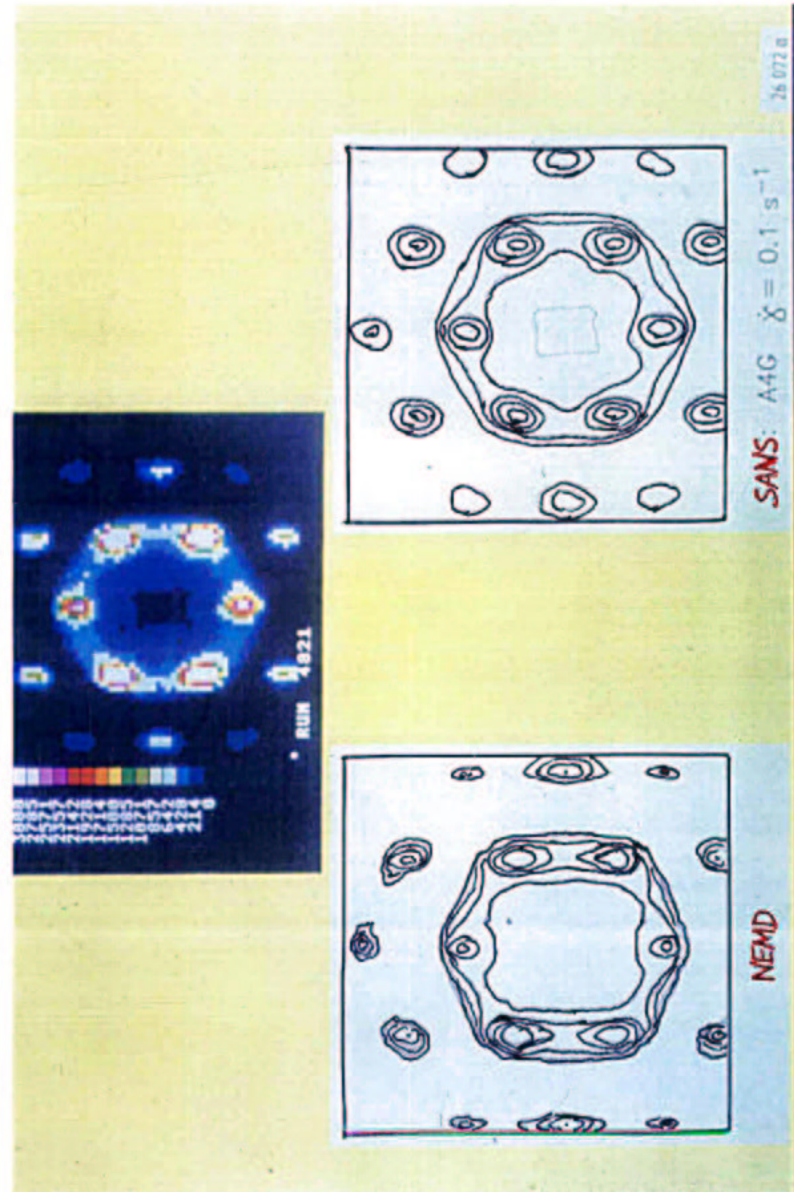
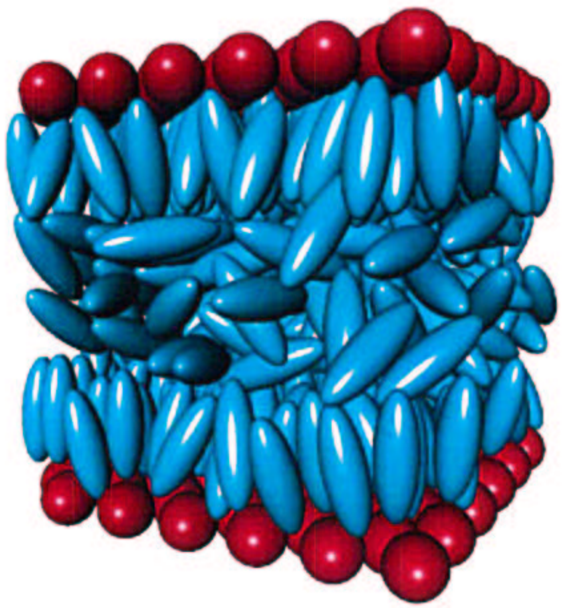
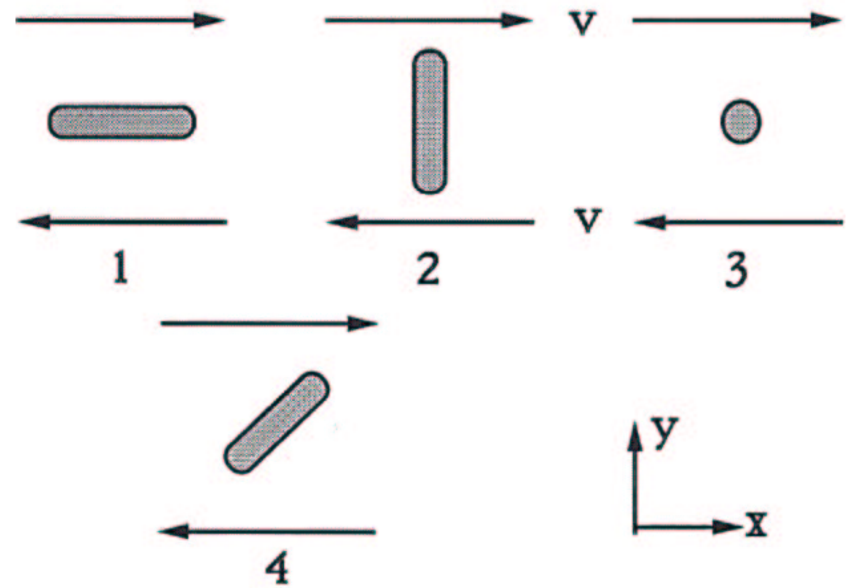
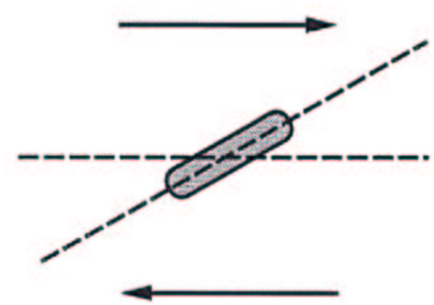

RUN 4821
SANS: A4G $\dot{\gamma} = 0.1\ s^{-1}$
NEMD

Materialeigenschaften von Flüssigkristallen



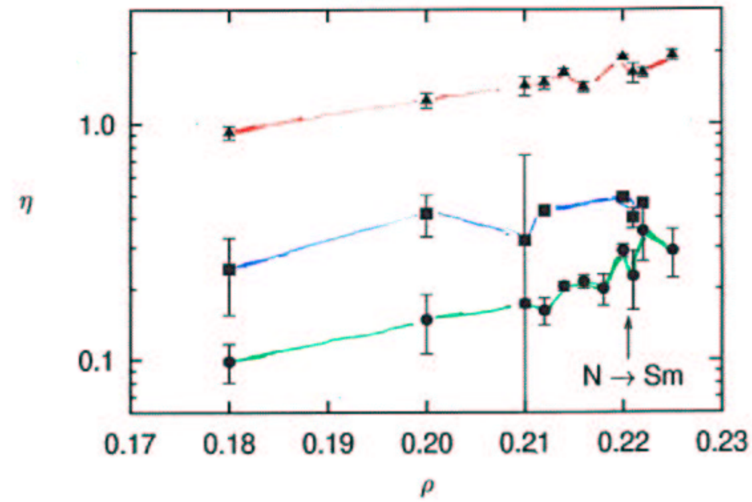


Field directions for Miesowicz viscosities



Flow alignment

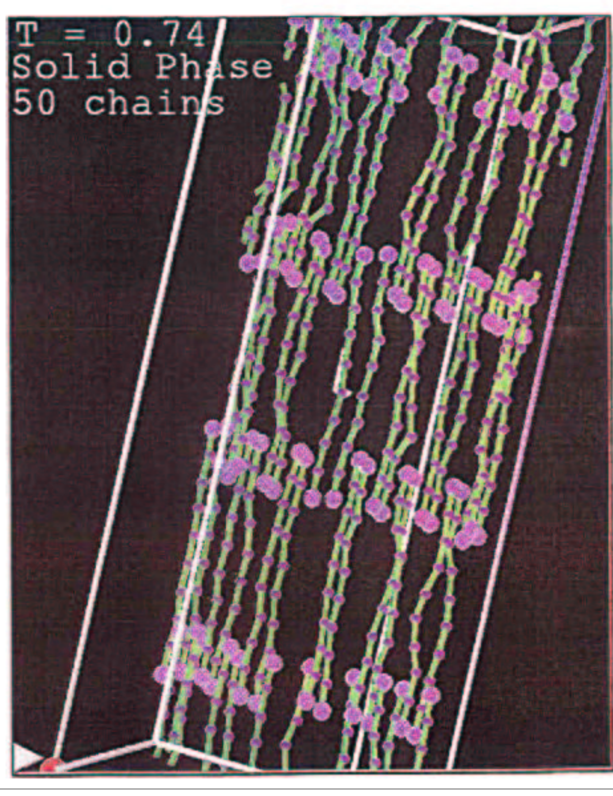
Miesowicz Viscosities as Functions of Density

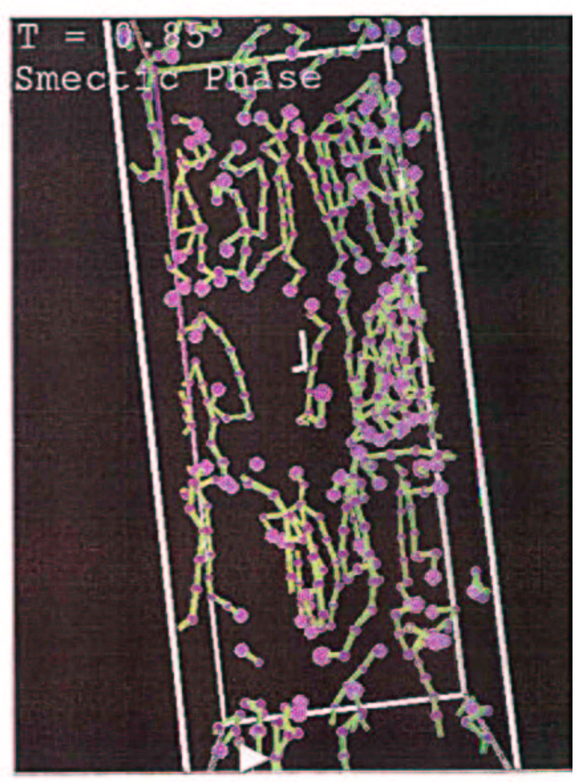


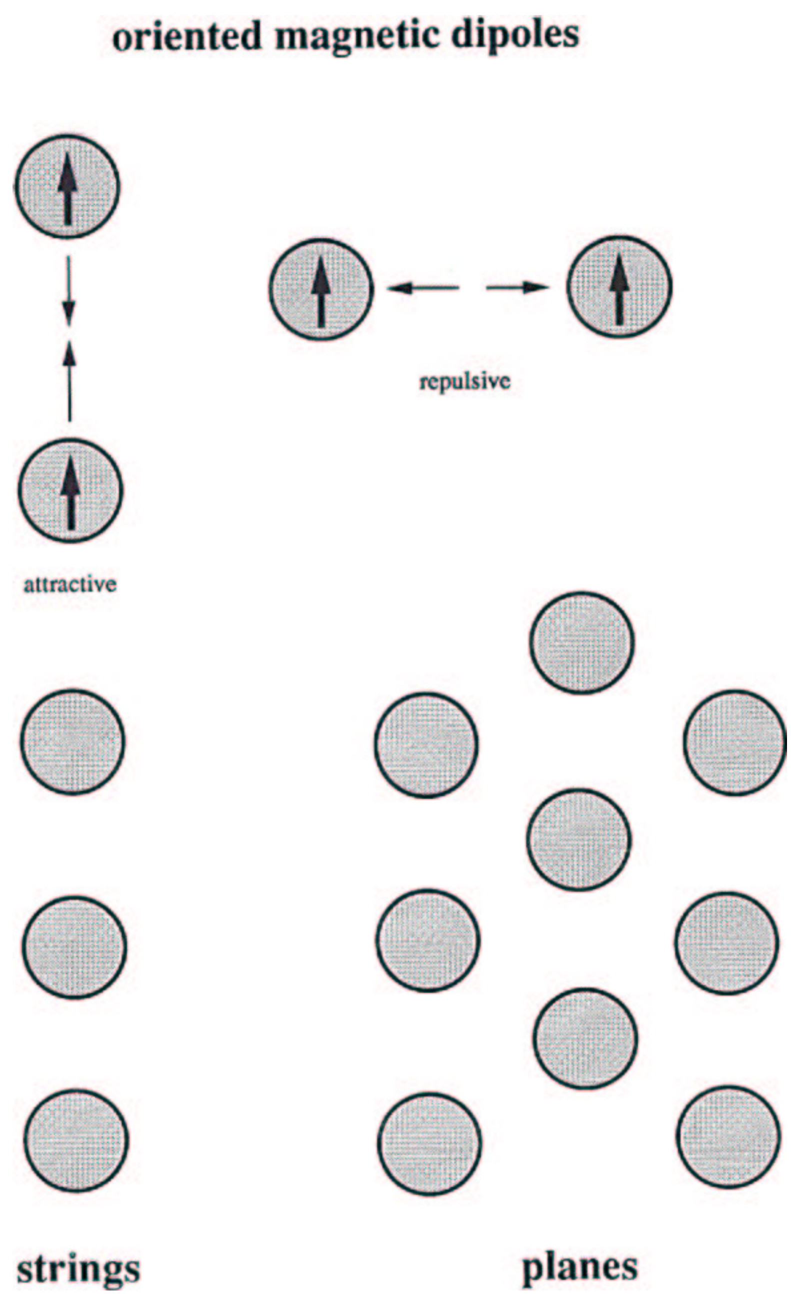
η_1 (●), η_2 (▲), and η_3 (■) as functions of density for $T = 0.95$ with $B = 0.9$.

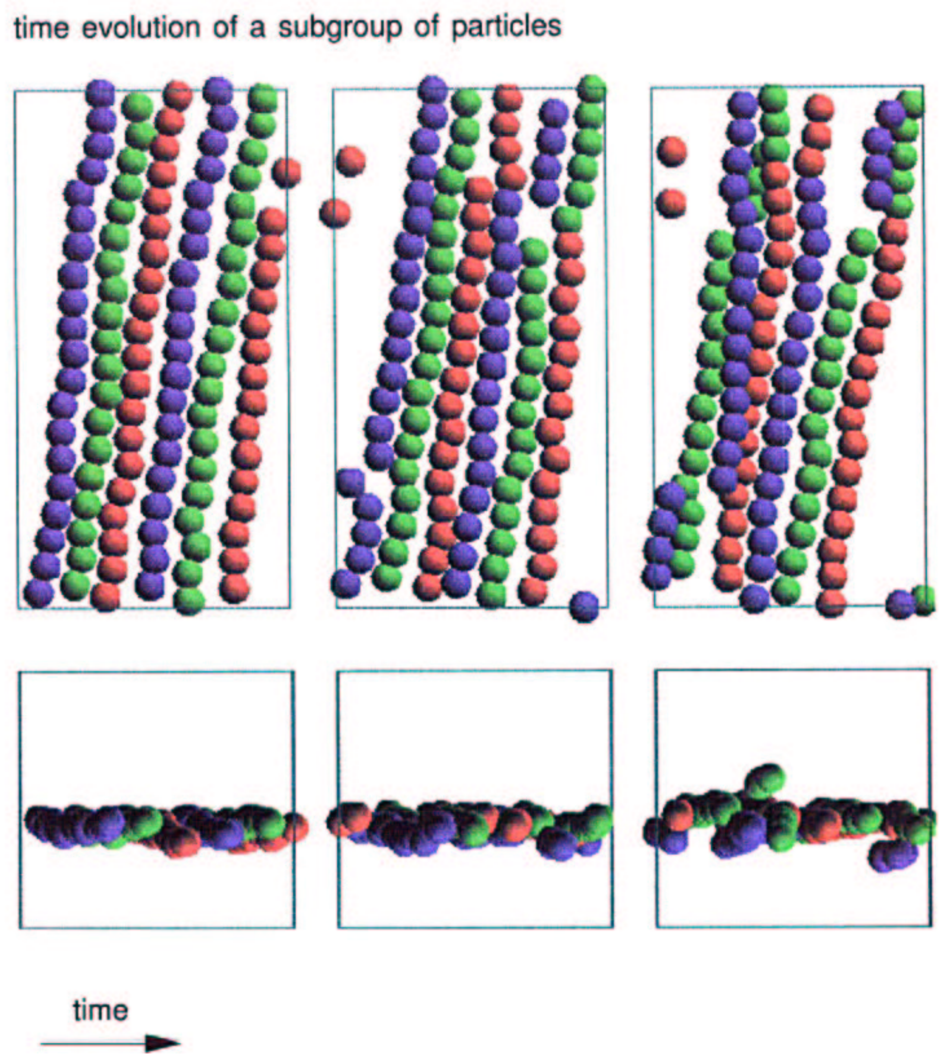
Institute for Theoretical Physics, Technical University of Berlin

Loris Bennett






oriented magnetic dipoles
repulsive
attractive
strings
planes

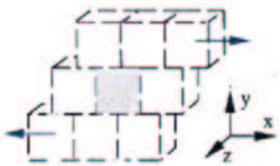

time evolution of a subgroup of particles
time

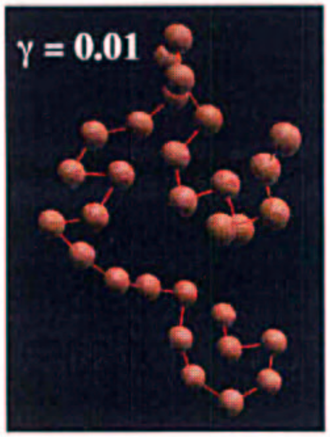
Conformations in sheared polymer melts

Theorie Exp. Sim.

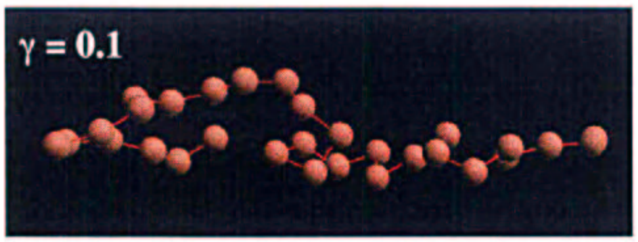
stationary flow regime

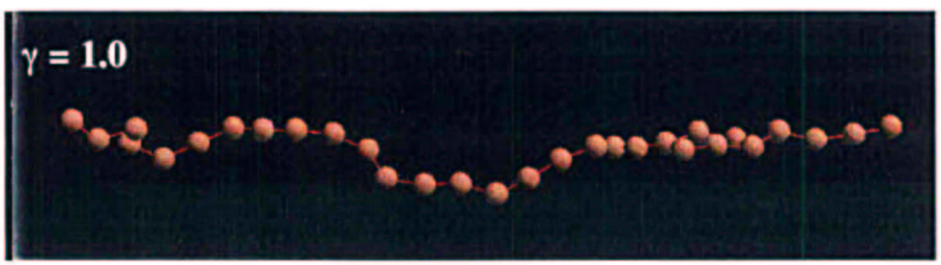
shear rate γ





viscosity decrease

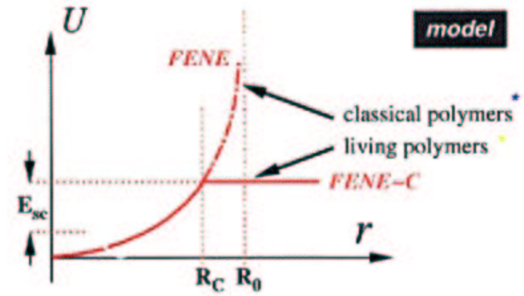




Microscopic models

Theorie Exp. Sim.

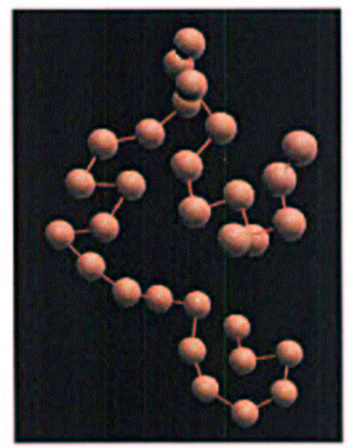
model



$$U^{bond} = U^{LJ} + U^{FENE-C}$$

Nonequilibrium molecular dynamics computer simulation

NEMD



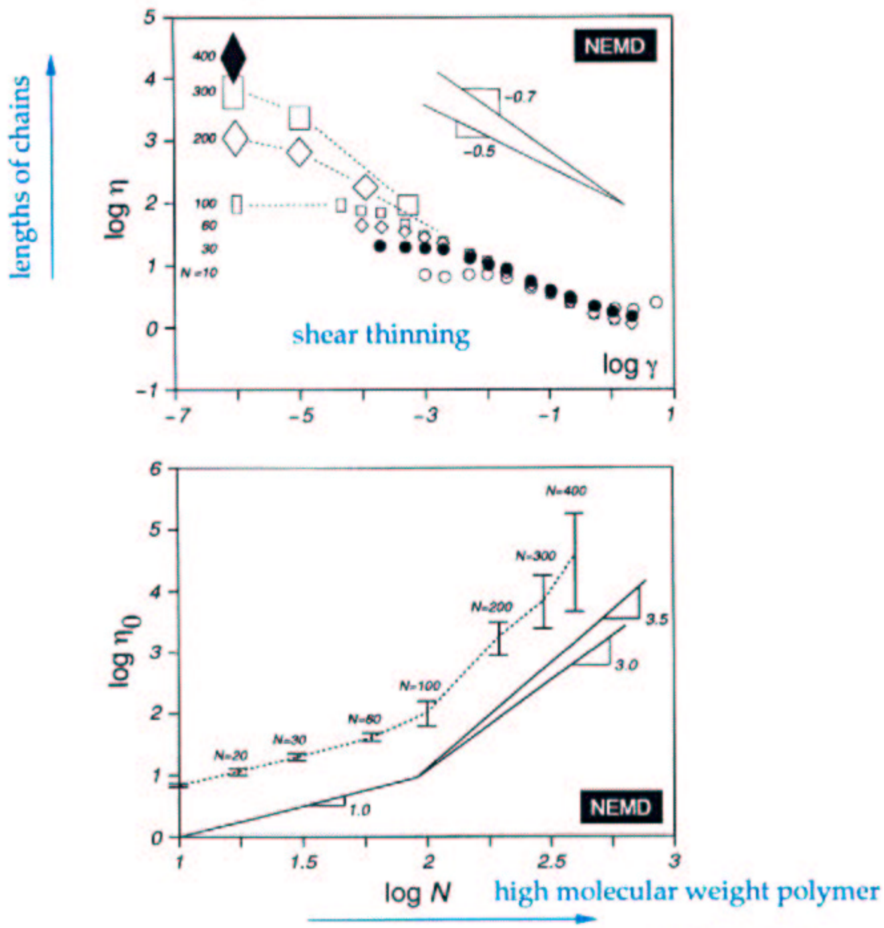
typical: 30000 monomers (Kuhn segments)

* M. Kröger , W. Loose and S. Hess, J. Rheology **37** (1993) 1057

* M. Kröger and R. Makhloufi, Phys. Rev. E **53** (1996) 2531

Rheological quantities

shear viscosity η(γ)



M. Kröger, Rheology 95 5 (1995) 66–71

M. Kröger, S.H. PRL 85 1128 (2000)

Static structure factors

of single chains

low shear rate
γ = 0.1

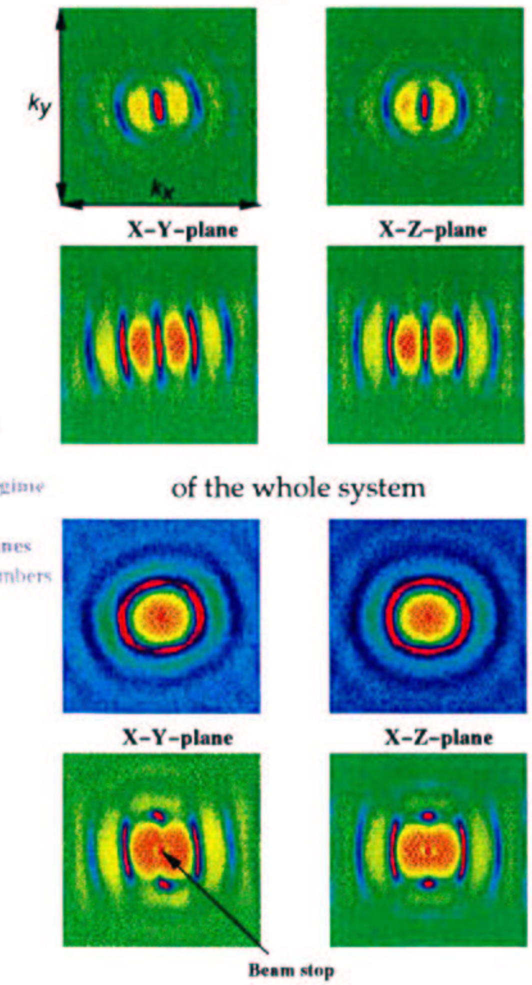
high shear rate
γ = 2.0

chain length = 30
8400 monomers
stationary flow regime
two shear rates
two scattering planes
(0,18.4) → wave numbers

of the whole system

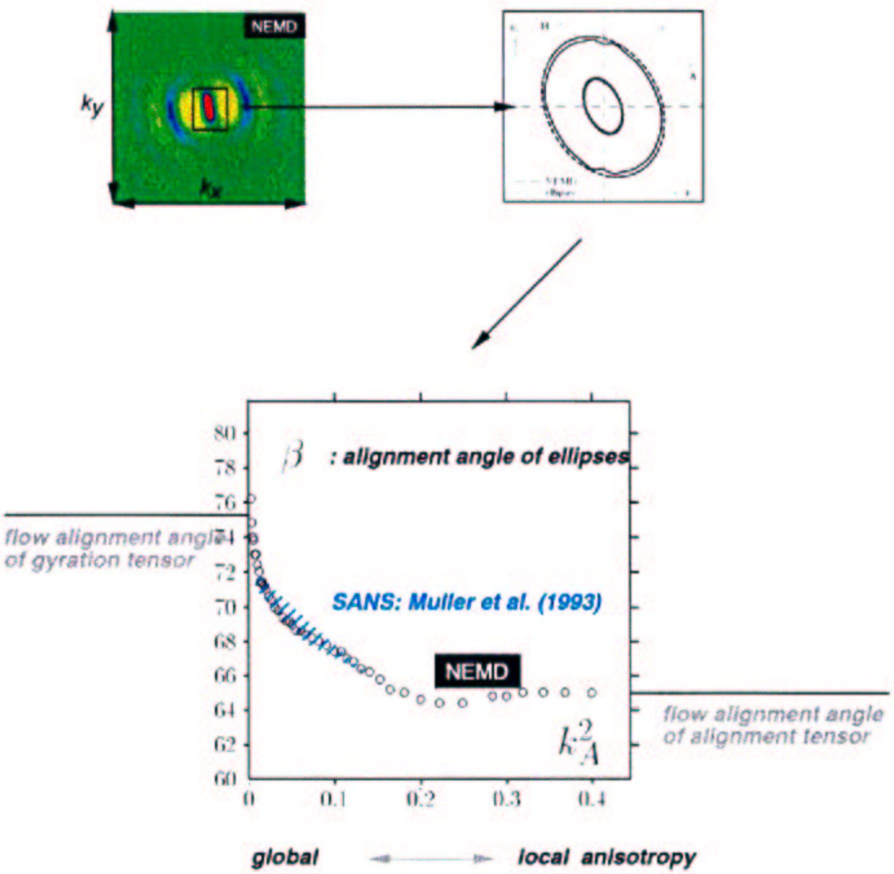
low shear rate
γ = 0.1

high shear rate
γ = 2.0



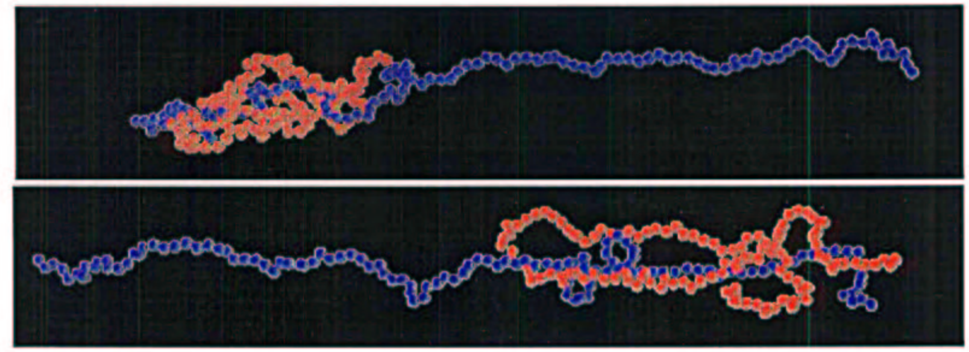
Anisotropy of the structure factor

– of single chains

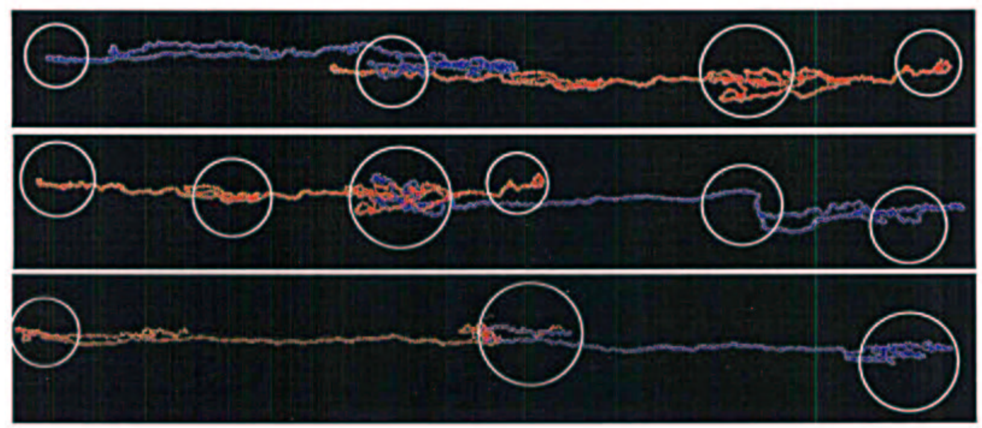


M. Kröger, W. Loose und S. Hess, J. Rheology **37** (1993) 1057–1080

Kettenlänge N = 120
Dehnung ε=4



Kettenlänge N = 480
Dehnung ε=4



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