FOR1394 DFG Research Unit
Nonlinear Response
to Probe Vitrification

Higher harmonics in sheared colloids: Divergence of the nonlinear response

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Japan-France Joint Seminar, YITP, Kyoto 2015

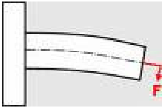
Maxwell Model of linear response

Viscous flow

$$\sigma_{xy} = \eta \frac{\partial v_x}{\partial y}$$

stress, viscosity, velocity gradient

Hookian elasticity



$$\sigma_{xy} = G_\infty \frac{\partial u_x}{\partial y}$$

stress, elastic constant, strain

Visco-elasticity (J.C. Maxwell, 1867)

$$\sigma_{xy}(t) = \int_{-\infty}^{t} dt' \; G(t-t') \; \frac{\partial v_x(t')}{\partial y}$$

$$G(t) = G_\infty \, e^{-t/\tau}$$

Fluid: $G(t)$ rapid

$$G(t) = \eta \, \delta(t) \, , \quad \eta = G_\infty \, \tau$$

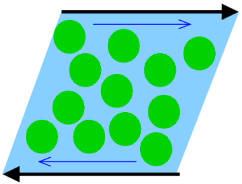
Solid: $G(t)$ slow

$$G(t) = G_\infty$$

Nonlinear response: FT Rheology

Non-time translational invariant $G(t,t')$

$$\sigma(t) = \int_{-\infty}^{t} dt' \, \dot{\gamma}(t') \, G(t,t')$$

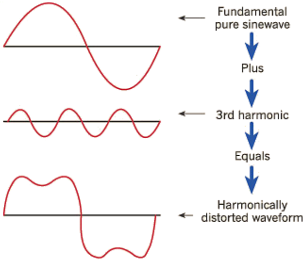


For the special case of oscillatory shear:

Input: $\gamma(t) = \gamma_0 \sin(\omega t)$

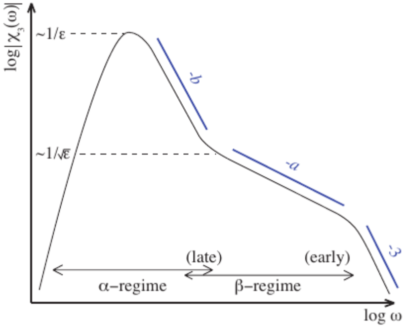
Output:

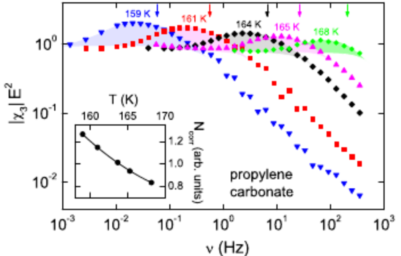
$$\sigma(t) = \gamma_0 \sum_{n=1}^{\infty} G'_n(\omega) \sin(n\omega t)$$
$$+ \gamma_0 \sum_{n=1}^{\infty} G''_n(\omega) \cos(n\omega t)$$



[fig: http://gain11.wordpress.com/2008/07/14/the-five-faces-of-distortion/]

3rd Harmonic & cooperativity





Biroli-Bouchaud theory*

- 3rd harmonic $\chi_3(\omega)$ diverges at glass transition
- $\chi_3(\omega) \propto \frac{\partial \chi_1(2\omega)}{\partial T}$

  (using: $T_c(E) = T_c(0) + \kappa\, E^2$, FDT)
- $\chi_3 \propto N_{\mathrm{corr}}$ (number of correlated particles)

Dielectric spectroscopy**

- $\chi_3(\omega)$ & N_{corr} measured

[⋆ Tarzia, Biroli, Lefevre & Bouchaud JCP **132**, 054501 (2010)]; also Biroli & Bouchaud, PRB **72** 064204 (2005)]

[⋆⋆ Bauer, Lunkenheimer & Loidl, PRL **111**, 225702 (2013); also Crauste-Thibierge, Brun, Ladieu, L'Hote, Biroli, Bouchaud, PRL **104**, 165703 (2010)]

Outline

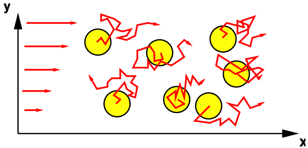
- Nonlinear
  - Dielectric Response
  - Biroli-Bouchaud Theory
- Large Amplitude Oscillatory Shear (LAOS) strain
  - Constitutive Equations in MCT-ITT
  - Fourier Transform Rheology
- 3rd Harmonic Spectrum
  - Scaling Laws
  - Experiment
- Summary
  - Nonlinear response of glass

Large Amplitude Oscillatory Shear

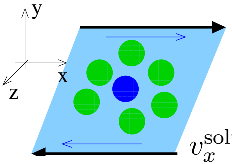
Constitutive Equations in MCT-ITT

Microscopic model

Brownian particles in flow



e.g. simple shear



$v_x^{\mathrm{solv}} = \dot{\gamma}(t)\, y$

Coupled random walks

$$\zeta \left(\frac{d}{dt}\mathbf{r}_i - \mathbf{v}^{\mathrm{solv}}(\mathbf{r}_i) \right) = \mathbf{F}_i + \mathbf{f}_i$$

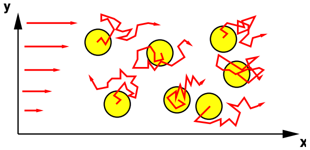
- homogeneous flow $\mathbf{v}^{\mathrm{solv}}(\mathbf{r}) = \boldsymbol{\kappa} \cdot \mathbf{r}$
- $\mathbf{F}_i$ interparticle force
- $\mathbf{f}_i$ random force

$$\langle f_i^{\alpha}(t)\, f_j^{\beta}(t') \rangle = 2\zeta k_B T \delta_{\alpha\beta}\delta_{ij}\delta(t-t')$$

Generalized Green Kubo relation (+ MCT approximation)

$$\boldsymbol{\sigma}(t) = \int_{-\infty}^{t} dt' \ \langle \mathrm{Tr}\{\boldsymbol{\kappa}(t)\cdot\boldsymbol{\sigma}\}\, e_{-}^{\int_{t'}^{t} ds\, \Omega^{\dagger}(s)}\, \boldsymbol{\sigma} \rangle^{(e)} / (k_B T V)$$

Brownian particles in flow



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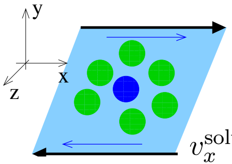

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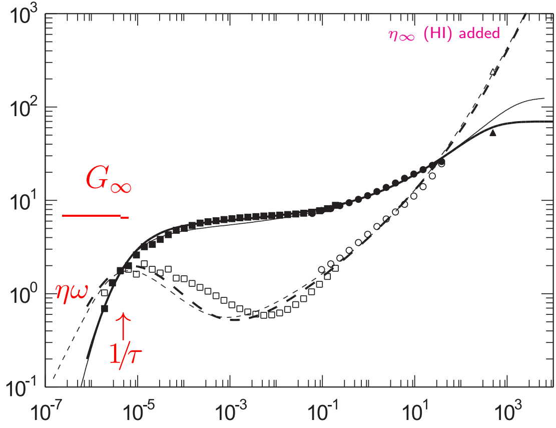
Linear rheology in colloids

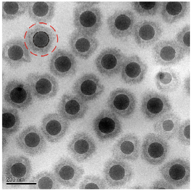
Linear response moduli



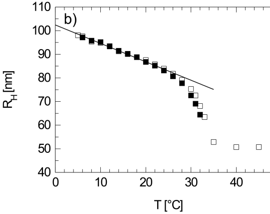
[Siebenbürger, Ballauff (2009)]

$\phi_{\rm eff} = \frac{4\pi}{3} R_H^3 \frac{N}{V} \approx 0.63$

PNIPAM microgels



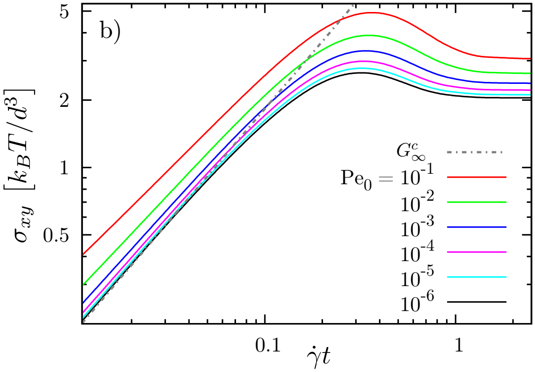
radius $R_{\rm H}(T)$



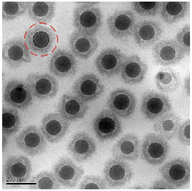
stress magnitudes with 50% error

Nonlinear rheology in colloids

Stress-strain relation in glass



PNIPAM microgels



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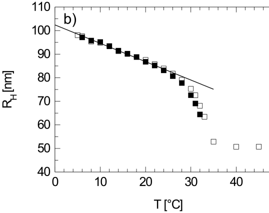
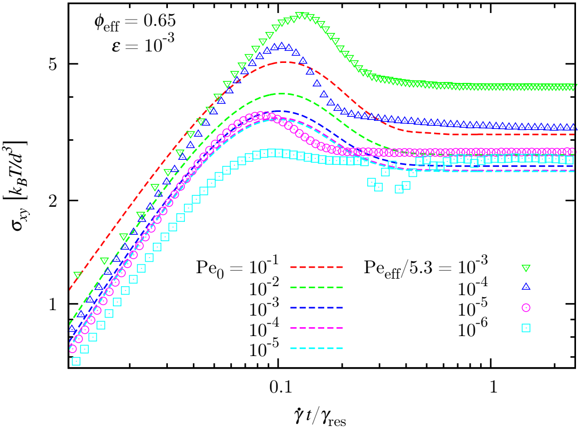


scaling-law for $\dot\gamma \to 0$ (theo.)

Nonlinear rheology in colloids

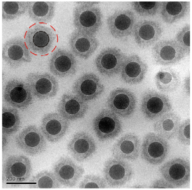
Stress-strain relation in glass



Siebenbürger, Ballauff [JPCM **27**, 194121 (2015)]

$$\mathrm{Pe}_0 = \dot\gamma \frac{R_H^2}{D_0}$$

PNIPAM microgels



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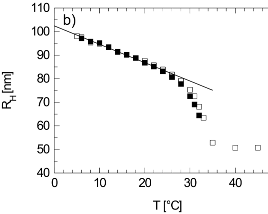
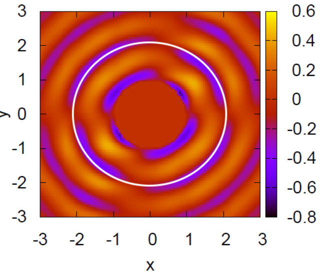


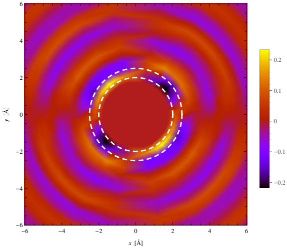
yield strain γ_* underestimated (factor 3)

Distorted structure

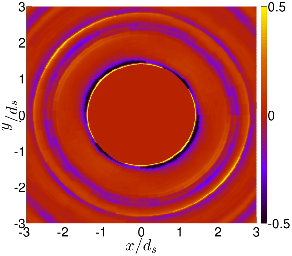
MCT-ITT



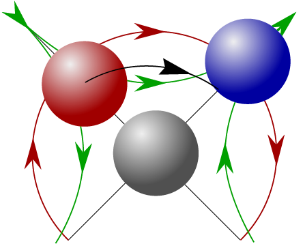
$d = 3$ MD metal melt*

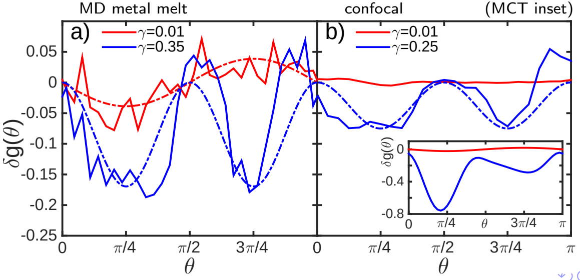


$d = 2$ BD hard disks



plastic deformation ($l = 4$)





$*$ P. Kuhn, Th. Voigtmann; $**$ M. Laurati, S. Egelhaaf] (unpublished, 2015

3rd Harmonic Spectrum

Scaling Laws

Experiment

schematic model used

[J. Brader, T. Voigtmann, MF, R. Larson and M. Cates, PNAS, **106**, 15186 (2009)]

LAOS-model

stress for applied shear rate $\dot\gamma(t) = \gamma_0 \sin \omega t$

$$\sigma(t) = \int_{-\infty}^{t} dt'\; G(t,t')\; \dot\gamma(t')$$

generalized shear modulus

$$G(t,t') = v_\sigma \; \Phi^2(t,t')$$

schematic F_{12} model for strain $\gamma(t,t') = \int_{t'}^{t} ds\; \dot\gamma(s)$

$$\partial_t \Phi(t,t') + \Gamma \left(\Phi(t,t') + \int_{t'}^{t} \mathrm{d}s\, m(t,s,t') \partial_s \Phi(s,t') \right) = 0$$

memory kernel

$$m(t,s,t') = h(\gamma(t,s))\, h(\gamma(t,t')) \;\; \left(\nu_1(\varepsilon)\, \Phi(t,s) + \nu_2^c\, \Phi^2(t,s) \right)$$

strain decorrelation

$$h(\gamma) = \frac{1}{1 + (\gamma/\gamma_*)^2}$$

Oscillatory shear – FT Rheology

dimensionless parameters:

shear rate: $\text{Pe}_0 = \dot{\gamma} \frac{R_H^2}{D_0}$ (bare Peclet number)

shear rate: $\text{Pe} = \dot{\gamma} \tau$ (Peclet, Weissenberg number)

frequency: $\text{Pe}_\omega = \omega \frac{R_H^2}{D_0}$

frequency: $\text{De} = \omega \tau$ (Deborah number)

stress: $\sigma \times \frac{R_H^3}{k_B T}$

strain: $\gamma = \frac{\gamma_0}{\gamma_*}$

Input:

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad , \quad \epsilon = \frac{\phi - \phi_c}{\phi_c}$$

(ϕ packing fraction)

Output:

$$\sigma(t) = \gamma_0 \sum_{n=1}^{\infty} G_n'(\omega) \sin(n \omega t) \; + \; \gamma_0 \sum_{n=1}^{\infty} G_n''(\omega) \cos(n \omega t)$$

Parameters: v_σ , Γ , γ_* & η_∞

Motivation

Object:
3rd Harmonic amplitude: $I_3 = |G_3(\omega)| \quad (\propto \gamma_0^2)$

$$Q_0 = \frac{1}{\gamma_0^2} \frac{I_3}{I_1}$$

Questions:

- Dependence on ω, ϵ ?
- I_3 related to $N_{\rm corr}$ (number of correlated particles) ?
- Plastic decay ?

Method:
Taylor approximation of schematic MCT model for $\gamma_0 \to 0$

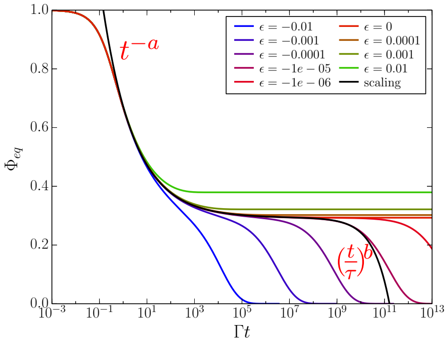
MCT's glass bifurcation

- glass transition ($\epsilon = 0$):
- glass stability analysis (β-scaling law)

$$\Phi_{eq}(t) \to f_c + \sqrt{|\epsilon|}\, g(t/t_\epsilon)$$

- α-scaling law ($\tau \sim (-\epsilon)^{-\gamma}$)

$$\Phi_{eq}(t) \to f_c\, \varphi(t/\tau)$$



functional: $\mathcal{S}[\Phi](t) = \int_0^t ds\ \{\Phi(s) - m(s) + m(s)\,\Phi(t-s)\} = 0$

bifurcation: $\left.\frac{\delta \mathcal{S}[\Phi](t)}{\delta \Phi(s)}\right|_{\Phi_{eq}=f_c} = \mathcal{O}(\epsilon, g^2)$

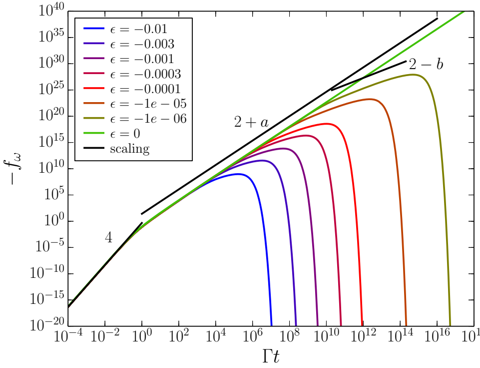
Nonlinear correlator at bifurcation

- Fourier expansion with $n = -1, 0, 1$

$$\frac{1}{\gamma_0^2}\left(\Phi(t,t') - \Phi_{eq}(t-t')\right) \to$$

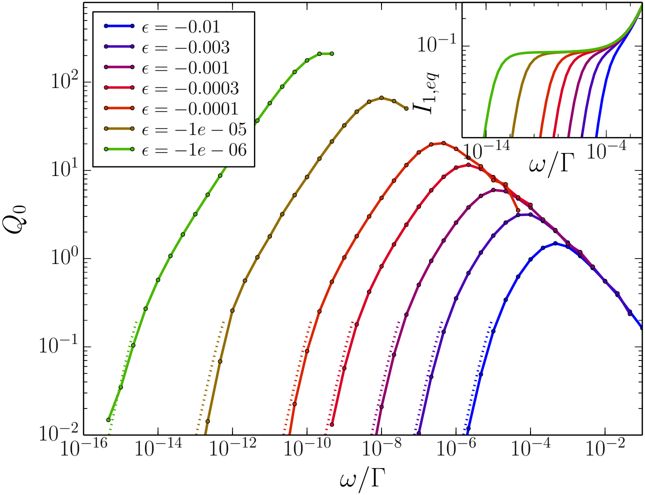
$$\sum_n f_n(t-t',\omega)\, e^{in\omega(t+t')}$$

- distortions f_n diverge for $\epsilon \to 0$
- f_n follow scaling-laws at fixed ωt
- $f_{n=0,\pm 1}(t, \omega \to 0) \propto \omega^2 f_\omega(t)$



expansion: $$\int_0^t ds \;\left.\frac{\delta \hat{\mathcal{S}}_{\omega,\star}[\Phi](t)}{\delta \Phi(s)}\right|_{\Phi = f_c + \sqrt{|\epsilon|}\, g} f_\star(s,\omega) = \frac{x_\star(\omega t)}{\sqrt{|\epsilon|}}$$

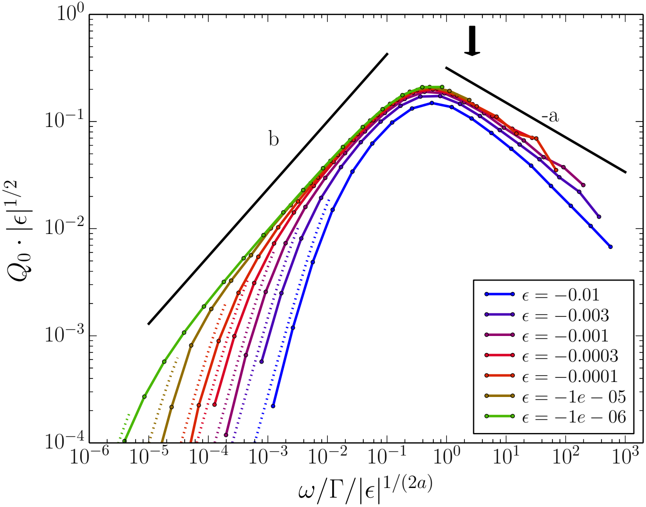
3rd Harmonic: theory



- $Q_0(\omega) = \frac{1}{\gamma_0^2} \frac{I_3}{I_1}$
- follows scaling laws for $\epsilon \to 0$

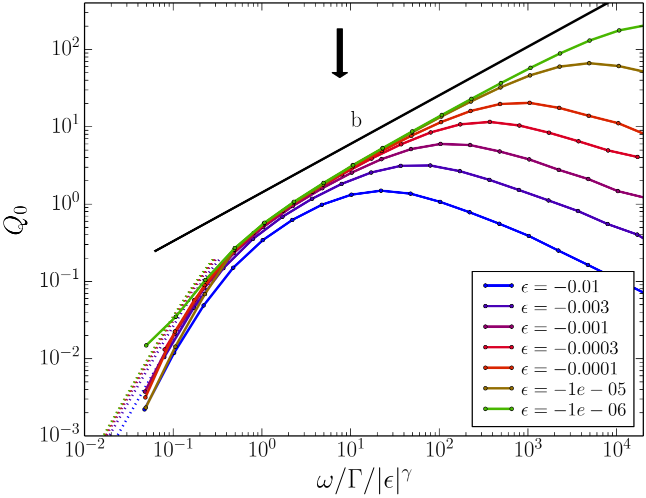
[equivalent to Tarzia, Biroli, Lefevre, Bouchaud (2010)]

3rd Harmonic: theory



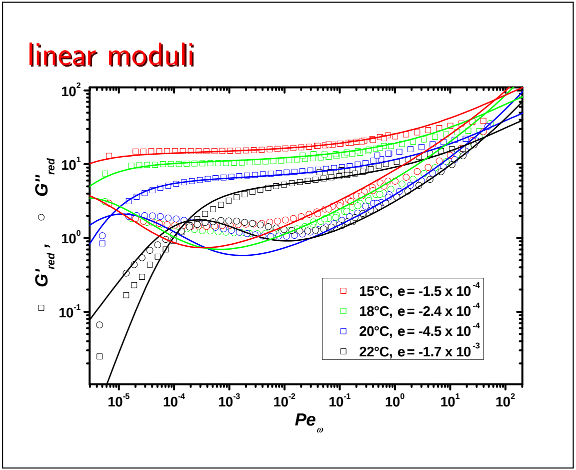
- $Q_0(\omega) = \frac{1}{\gamma_0^2} \frac{I_3}{I_1}$
- follows scaling laws for $\epsilon \to 0$
- β**-scaling law**
- maximum close to minimum in G''

3rd Harmonic: theory

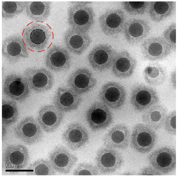


- $Q_0(\omega) = \frac{1}{\gamma_0^2}\,\frac{I_3}{I_1}$
- follows scaling laws for $\epsilon \to 0$
- α-scaling law
- shoulder close to $\omega \approx 1/\tau$

Comparison with experiment



- Expt.: PNIPAM microgels



(Siebenbürger, Ballauff, HZB)

- Fit of schematic MCT parameters only with linear response & steady stress curves

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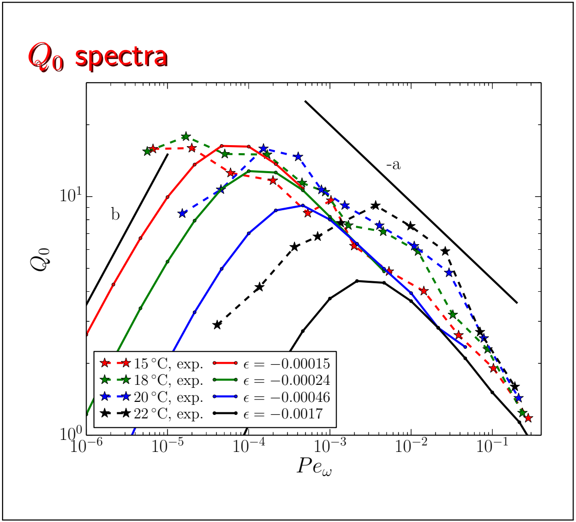
Experiment: Merger, Wilhelm, KIT

Comparison with experiment



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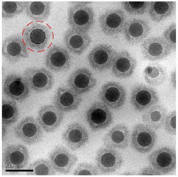

(Siebenbürger, Ballauff, HZB)

- β-scaling compatible
- different to dielectric $\chi^{(3)}(\omega)$

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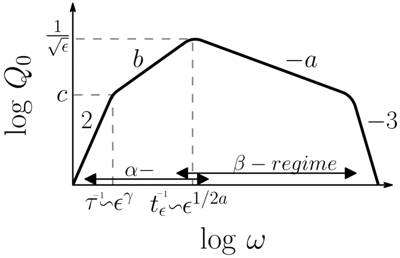
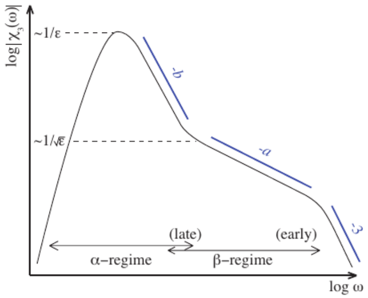
3rd harmonic under strain



- I_3 tests elasticity on β-scale
- no detailed balance in shear
- glass yields for $\dot{\gamma} \neq 0$

3rd harmonic in electric field



- χ_3 tests α- relaxation
- generalized FDR
- glass transition shifted $T_c(E) = T_c(0) + \kappa\, E^2$

Acknowledgements

- Rabea Seyboldt, Fabian Coupette
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- Miriam Siebenbürger, Matthias Ballauff (HZ Berlin)
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Thank you for your attention