Theory of heterogeneous viscoelasticity

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Maxwell's visco-elastic theory

J. C. Maxwell, Philos. Trans. Roy. Soc. 1867

Stress-Strain relation for a liquid and a solid

solid: $\sigma_{xz} = G\epsilon_{xz}$ $\leftarrow$ strain

liquid: $\sigma_{xz} = \eta v_{xz}$ $\leftarrow$ strain rate

$$\epsilon_{ij} = \tfrac{1}{2}(\nabla_i u_j + \nabla_j u_i) \qquad v_{ij} = \tfrac{1}{2}(\nabla_i v_j + \nabla_j v_i)$$

Superposition of "solid" and "liquid" strain rates:

$$v_{xz,\mathrm{eff}} = v_{xz} + \frac{d}{dt}\epsilon_{xz} \quad \Rightarrow$$

$$\frac{1}{\eta_{\mathrm{eff}}(\omega)} = \frac{i\omega}{G_{\mathrm{eff}}(\omega)} = \frac{1}{\eta} + \frac{i\omega}{G_\infty} = \frac{1}{G_\infty}\left(\frac{1}{\tau} + i\omega\right)$$

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G_∞ is the high-frequency shear modulus, $\tau = \eta/G_\infty$ is Maxwell’s relaxation time.

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- For times larger than τ the visco-elastic material acts like a solid.

$$\epsilon_{ij} = \frac{1}{2}(\nabla_i u_j + \nabla_j u_i) \qquad v_{ij} = \frac{1}{2}(\nabla_i v_j + \nabla_j v_i)$$

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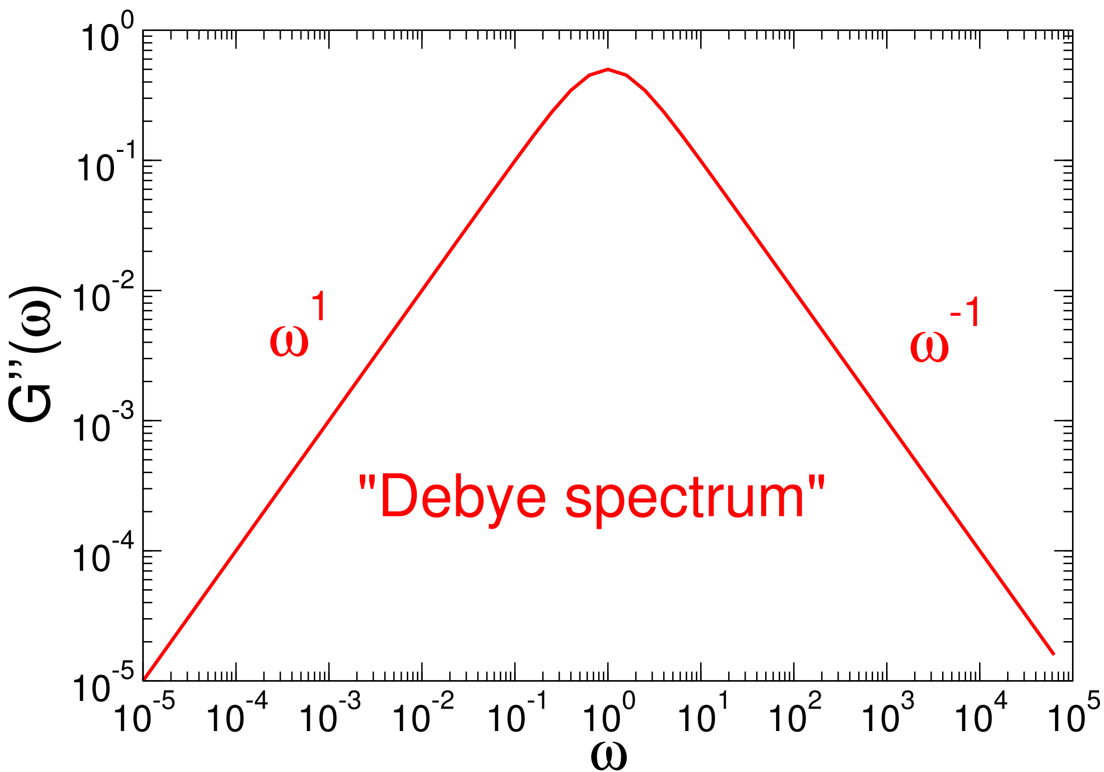
G_∞ is the high-frequency shear modulus, $\tau = \eta/G_\infty$ is Maxwell's relaxation time.

- For times larger than τ the visco-elastic material acts like a solid.
- If τ is larger than a glass-blower's time scale, the glass transition has occurred.

Maxwells visco-elastic theory

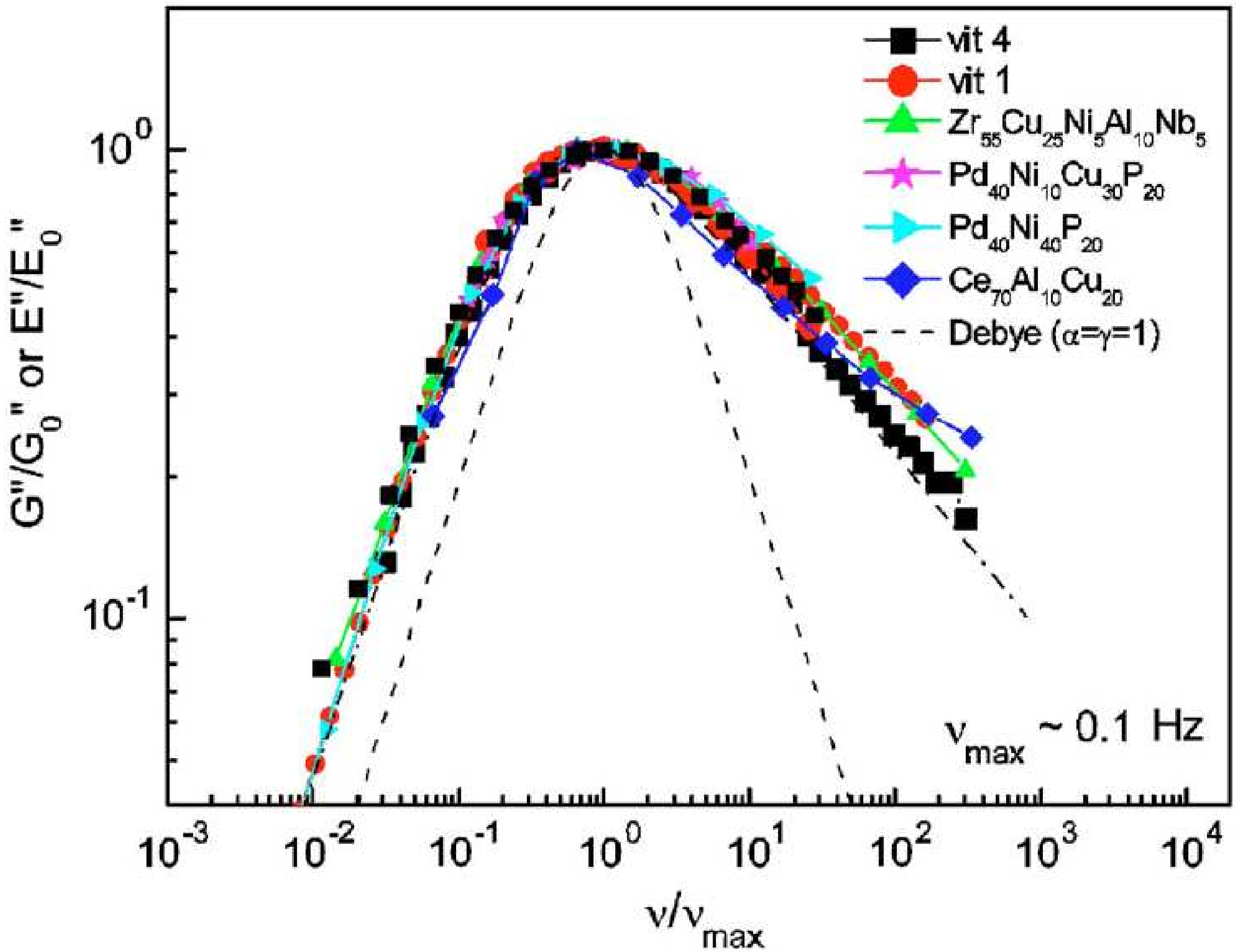
Consequence for the mechanical loss modulus $G''(\omega)$:

$$G''(\omega) = \mathrm{Im}\{G_{\mathrm{eff}}(\omega)\} = G_\infty \frac{\omega\tau}{1 + (\omega\tau)^2}$$



Mechanical relaxation spectra of metallic glasses

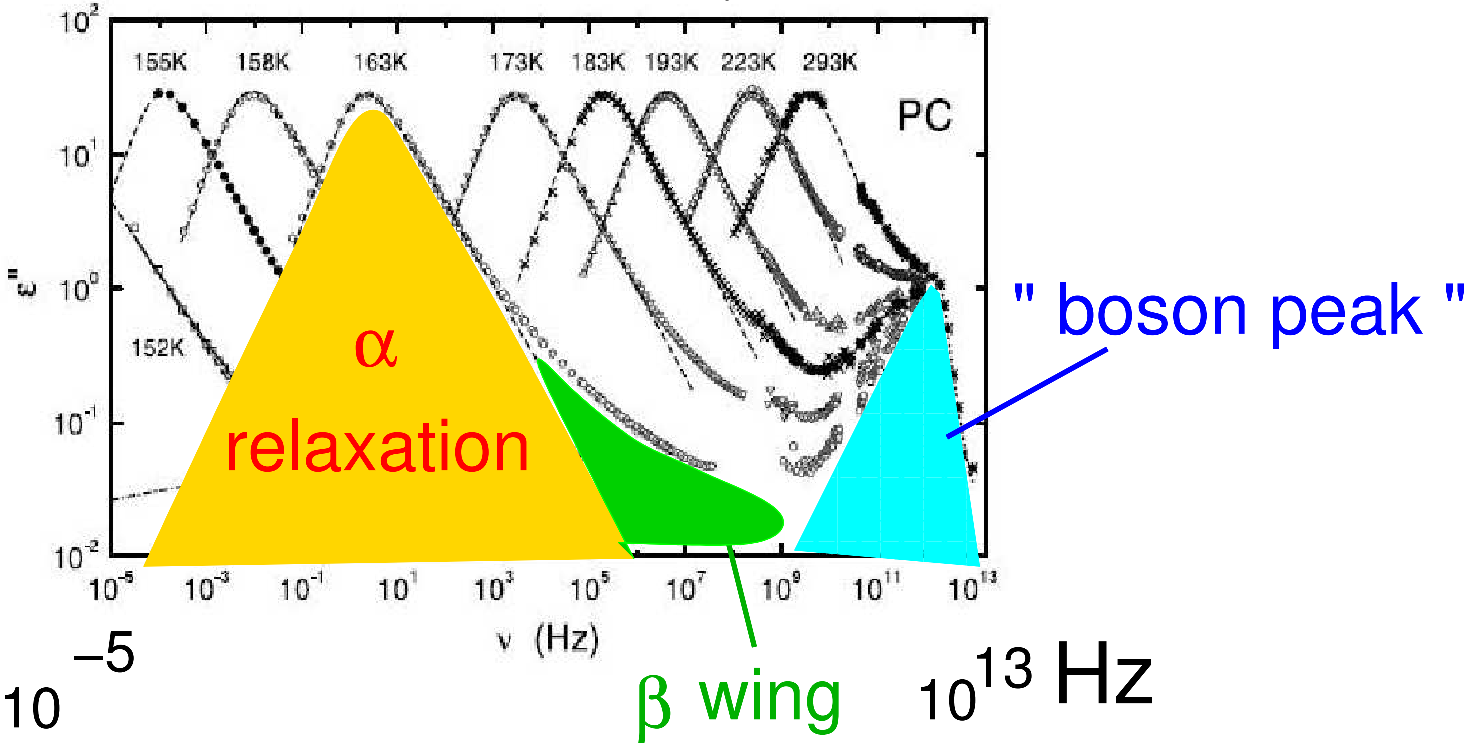
164503-2 Wang, Liu, and Wang J.Chem.Phys 2008



Typical Dielectric loss spectra of glasses

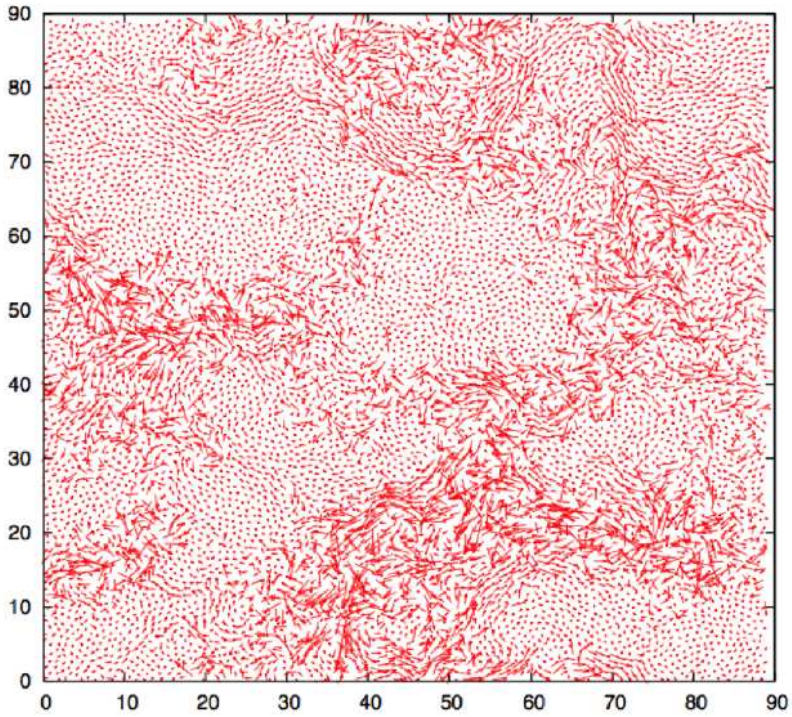
Poly-Carbonate (T_g = 420 K)

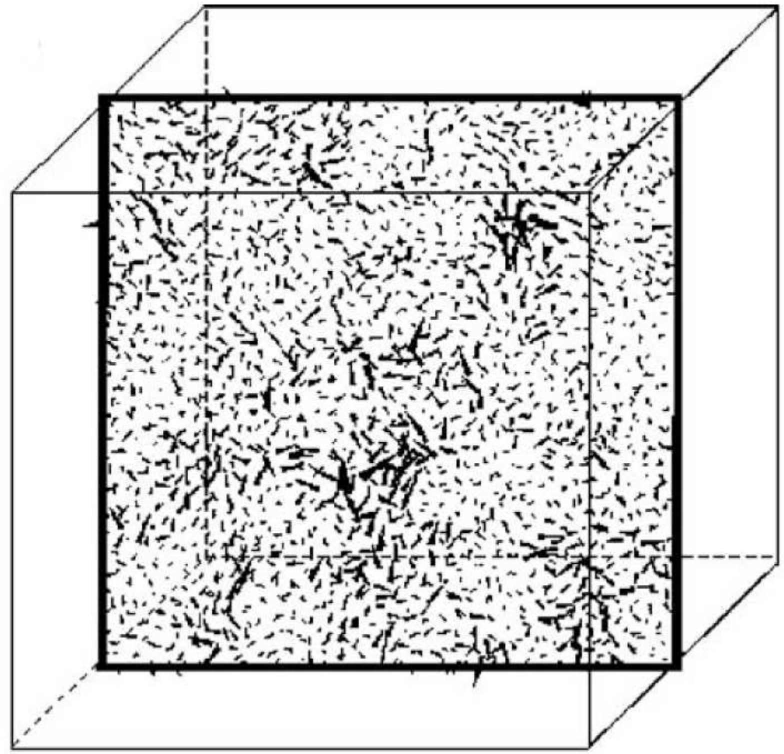
P. Lunkenheimer et al. J. Noncryst. Sol. 307–310, 336 (2002)



- In comparison with the mechanic loss spectra the dielectric ones tend to be more symmetric (if it were not for the "beta wing")

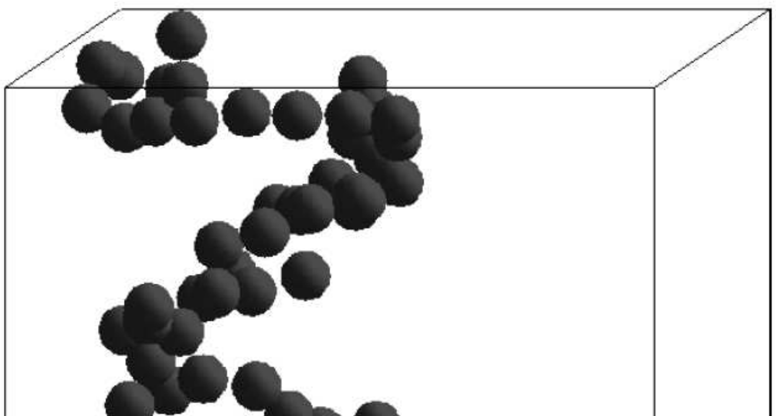
Dynamic and elastic heterogeneities in simulations of liquids/glasses

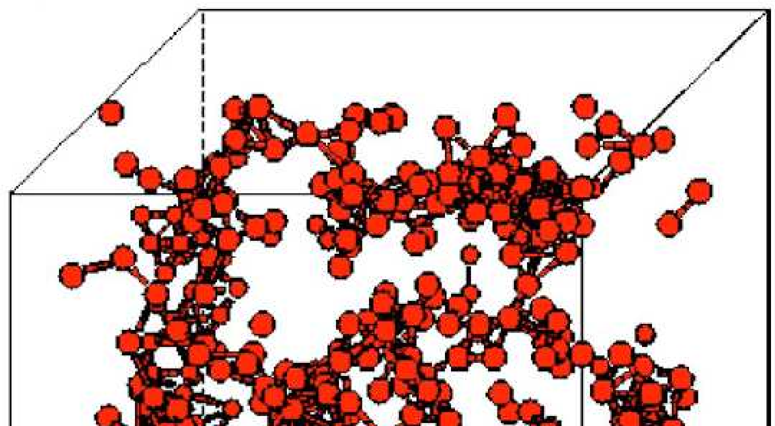


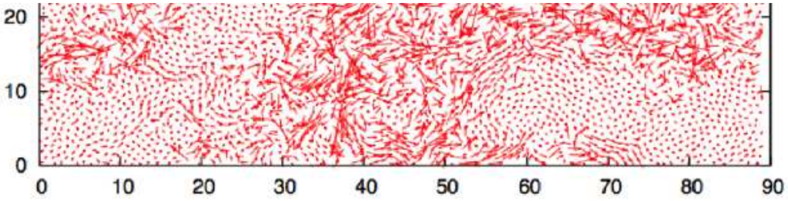


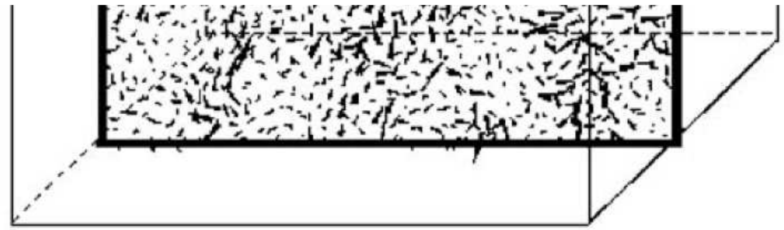
dynamical heterogenity (Berthier, Physics, 2011)

Elastic heterogeneity (Leonforte et al. PRB 2005



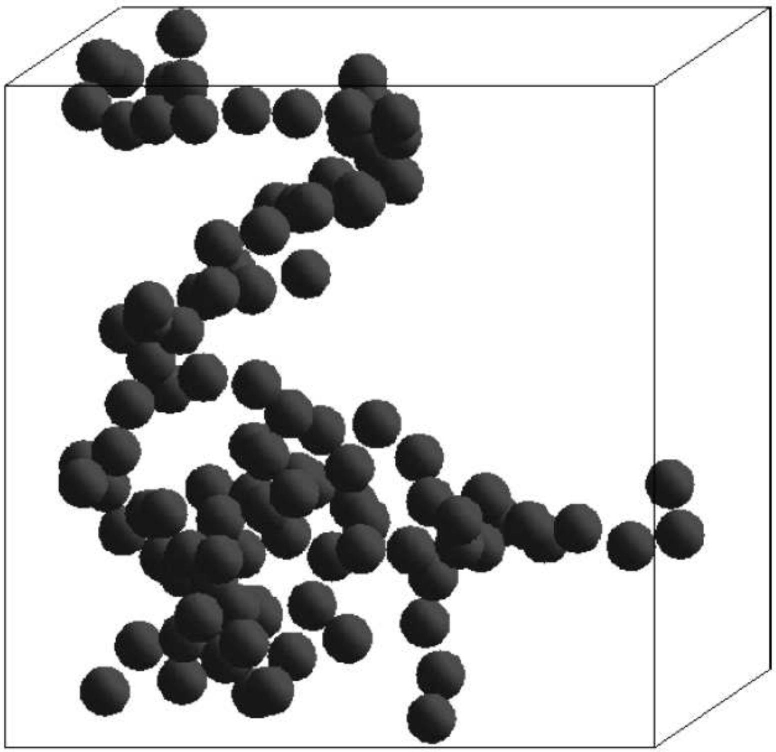


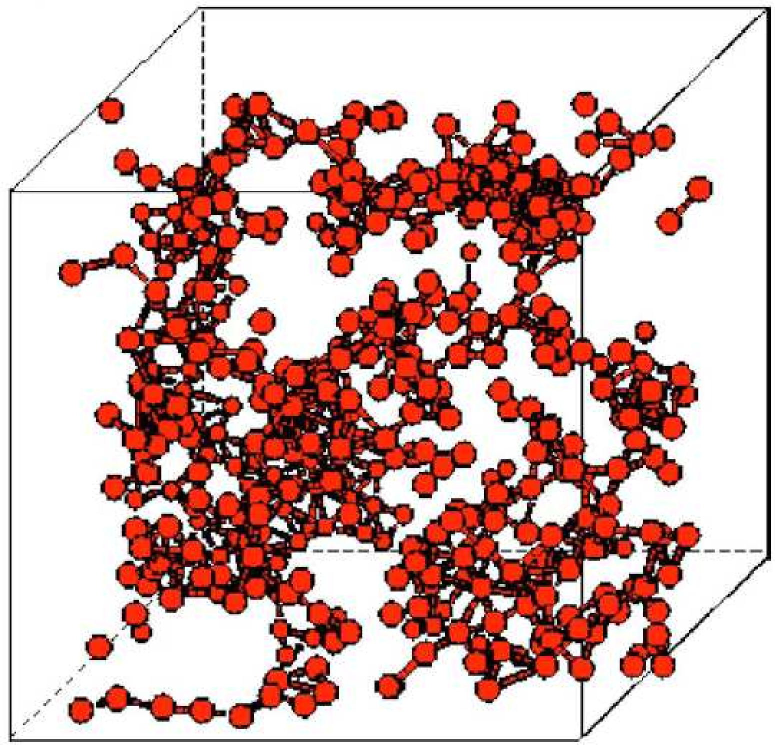




dynamical heterogenity (Berthier, Physics, 2011)

Elastic heterogeneity (Leonforte et al. PRB 200





Most mobile cluster (Glotzer, JNCS 2000)

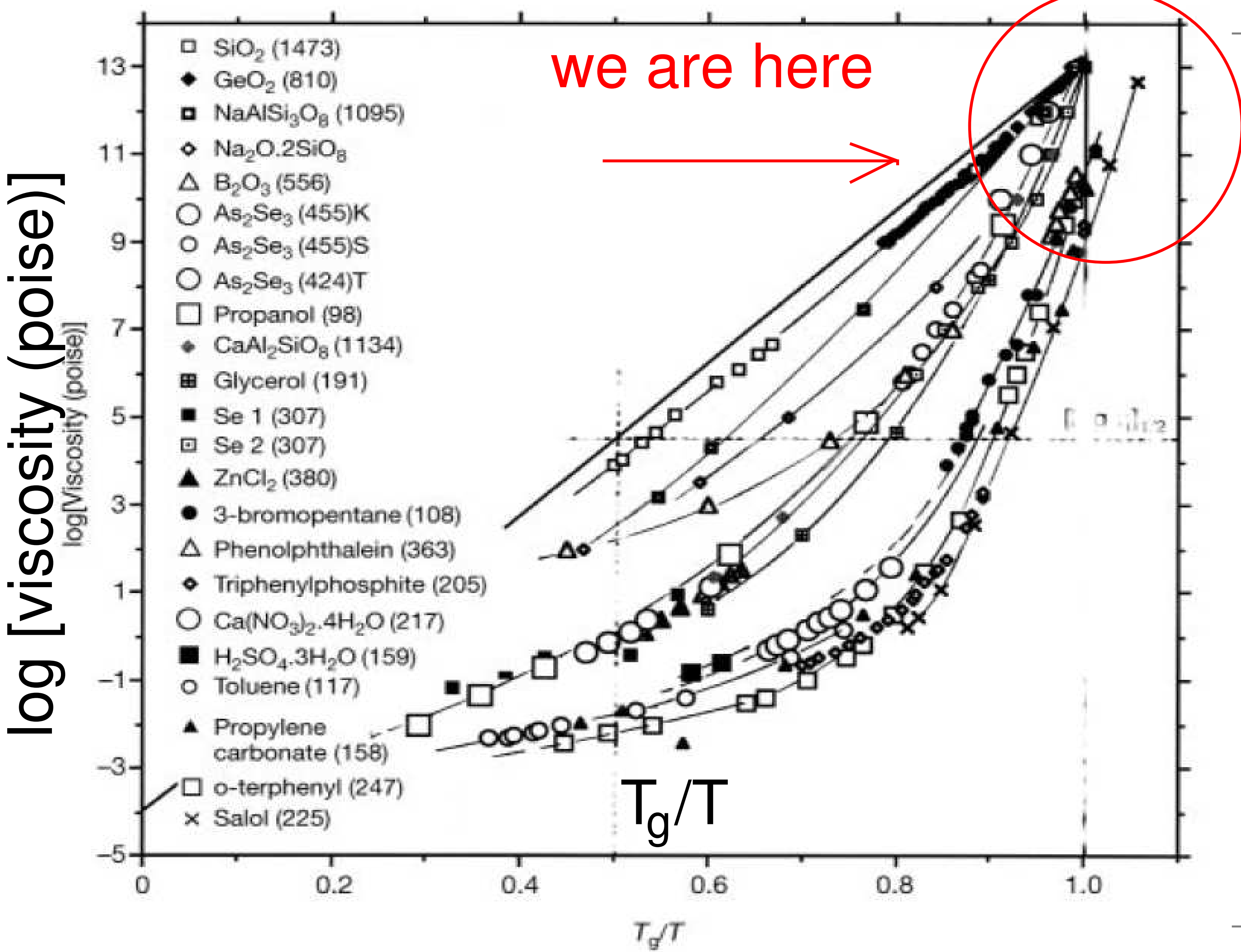
strongest non-affine cluster (Leonforte et al. PRB 2005

Heterogeneous visco-elastic model

W. Schirmacher, G. Ruocco, V. Mazzone, PRL 115, 015901 (2015)

- Start with linearized Navier-Stokes equation using Maxwell's effective viscosity
- Assume that the local shear modulus $G(\mathbf{r})$ and local viscosity $\eta(\mathbf{r})$ fluctuate in space (but are "frozen")
- Shoving-model relationship of J. Dyre between $G(\mathbf{r})$ and $\eta(\mathbf{r})$

Angell Plot of viscosities



Heterogeneous visco-elastic model

W. Schirmacher, G. Ruocco, V. Mazzone, PRL 115, 015901 (2015)

Linearized Navier-Stokes equations

with space and frequency-dependent local viscosity

$$i\omega\rho_m v_i(\mathrm{r},\omega) = \frac{K}{i\omega}\nabla^2 v_i + 2\sum_j \nabla_j \eta_{\mathrm{eff}}(\mathrm{r},\omega)\widehat{v}_{ij}(\mathrm{r},\omega)$$

$$v_{ij} = \tfrac{1}{2}(\nabla_i v_j + \nabla_j v_i) \qquad \widehat{v}_{ij} = v_{ij} - \tfrac{1}{3}\delta_{ij}\mathrm{Tr}\{v_{ij}\}$$

$$\frac{1}{\eta_{\mathrm{eff}}(\mathrm{r},\omega)} = \frac{i\omega}{G_{\mathrm{eff}}(\mathrm{r},\omega)} = \frac{1}{\eta(\mathrm{r})} + \frac{i\omega}{G(\mathrm{r})}$$

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- Assumption that $\ln\eta(\mathbf{r}) \propto E(\mathbf{r})$ and $G(\mathbf{r})$ are related: "shoving model" (J. Dyre et al. 1996)

Activation energy of $\eta(\mathbf{r})$:

$$E(\mathbf{r}) = V_A G(\mathbf{r})$$

- Meyer-Neldel compensation rule for the prefactor of $\eta(\mathbf{r})$

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Activation energy of $\eta(\mathbf{r})$:

$$E(\mathbf{r}) = V_A G(\mathbf{r})$$

- Meyer-Neldel compensation rule for the prefactor of $\eta(\mathbf{r})$

$\eta(\mathbf{r}) = \eta_0 e^{[E(\mathbf{r}) - TS(\mathbf{r})]/k_B T}$ $\qquad S(\mathbf{r})/k_B = \alpha E(\mathbf{r})$

$$\Rightarrow \eta(\mathbf{r}) = \eta_0 e^{E(\mathbf{r})\overbrace{\left[\frac{1}{k_B T} - \alpha\right]}^{\beta_{\text{eff}}}}$$

Coarse-grained Navier-Stokes equations

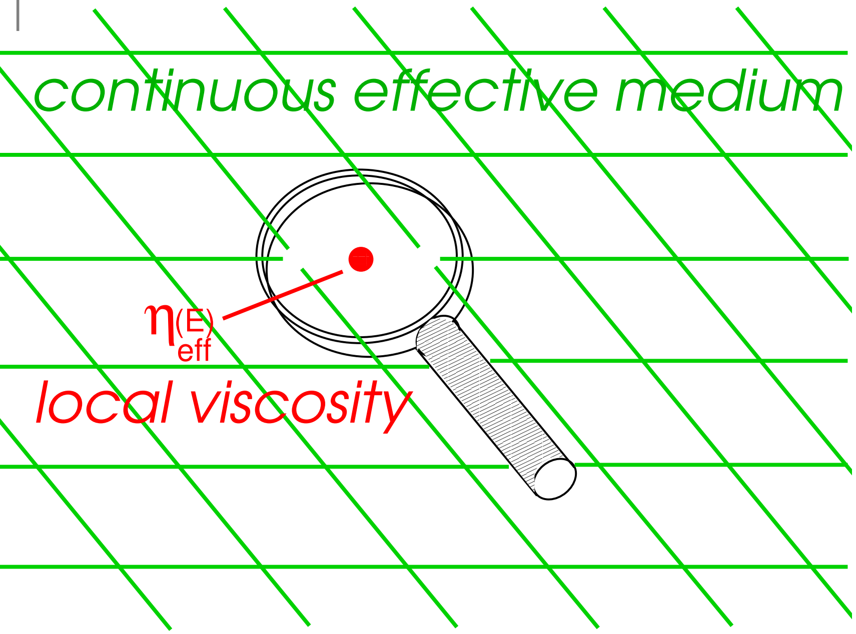
with macroscopic frequency-dependent viscosity

$$i\omega\rho_m v_i(\mathbf{r},\omega) = \frac{K}{i\omega}\nabla^2 v_i + 2\eta(\omega)\sum_j \nabla_j \widehat{v}_{ij}(\mathbf{r},\omega)$$

- The disorder leads to an additional frequency dependence
- The solution $\eta_{\mathrm{eff}}(\mathbf{r},\omega) \rightarrow \eta(\omega)$ is obtained via the coherent-potential approximation (CPA) using a Gaussian statistics of $E(\mathbf{r})$.

CPA for the spatially fluctuating viscosity

W. Schirmacher et al., PRL 115, 015901 (2015)



obeying the coarse-grained Navier-Stokes equation for $\eta(\omega)$

Self-consistent CPA condition:

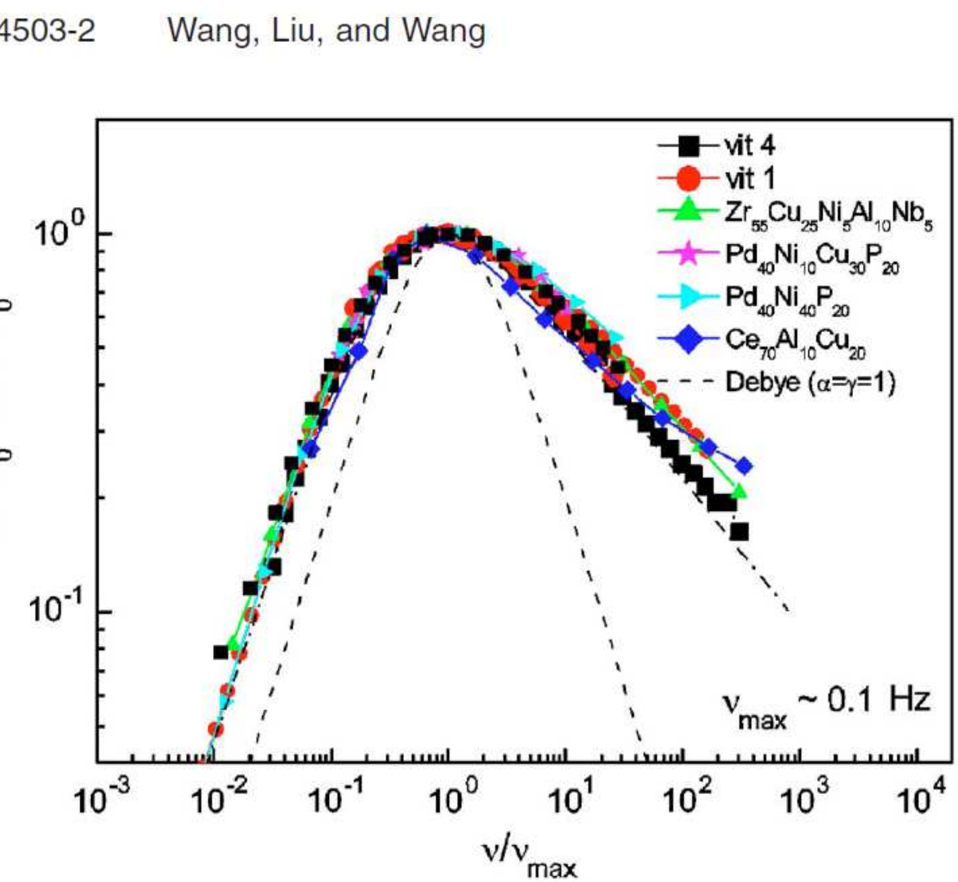
$$\left\langle \frac{\eta(\omega) - \eta_{\text{eff}}(E, \mathbf{r}, \omega)}{1 - \frac{2\nu}{3}[\eta(\omega) - \eta_{\text{eff}}(E, \mathbf{r}, \omega)]/\eta(\omega)} \right\rangle_E = 0$$

The scattering T matrix due to the "perturbation" induced by replacing the macroscopic by the microscopic viscosity should be – on the average – zero.

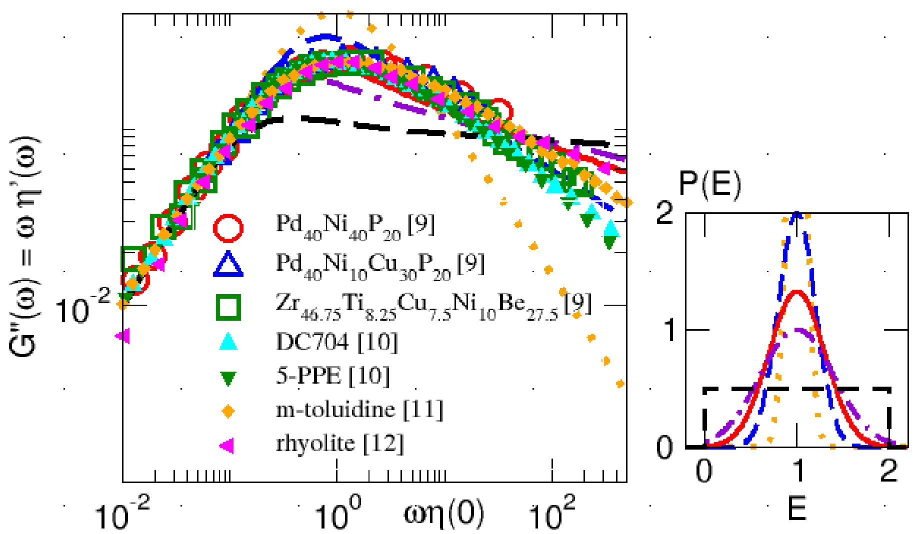
- Derived as saddle-point of replica field theory

S. Köhler et al., PRB 88, 064203 (2013)

Relaxation data in supercooled liquid metals and viscosity CPA



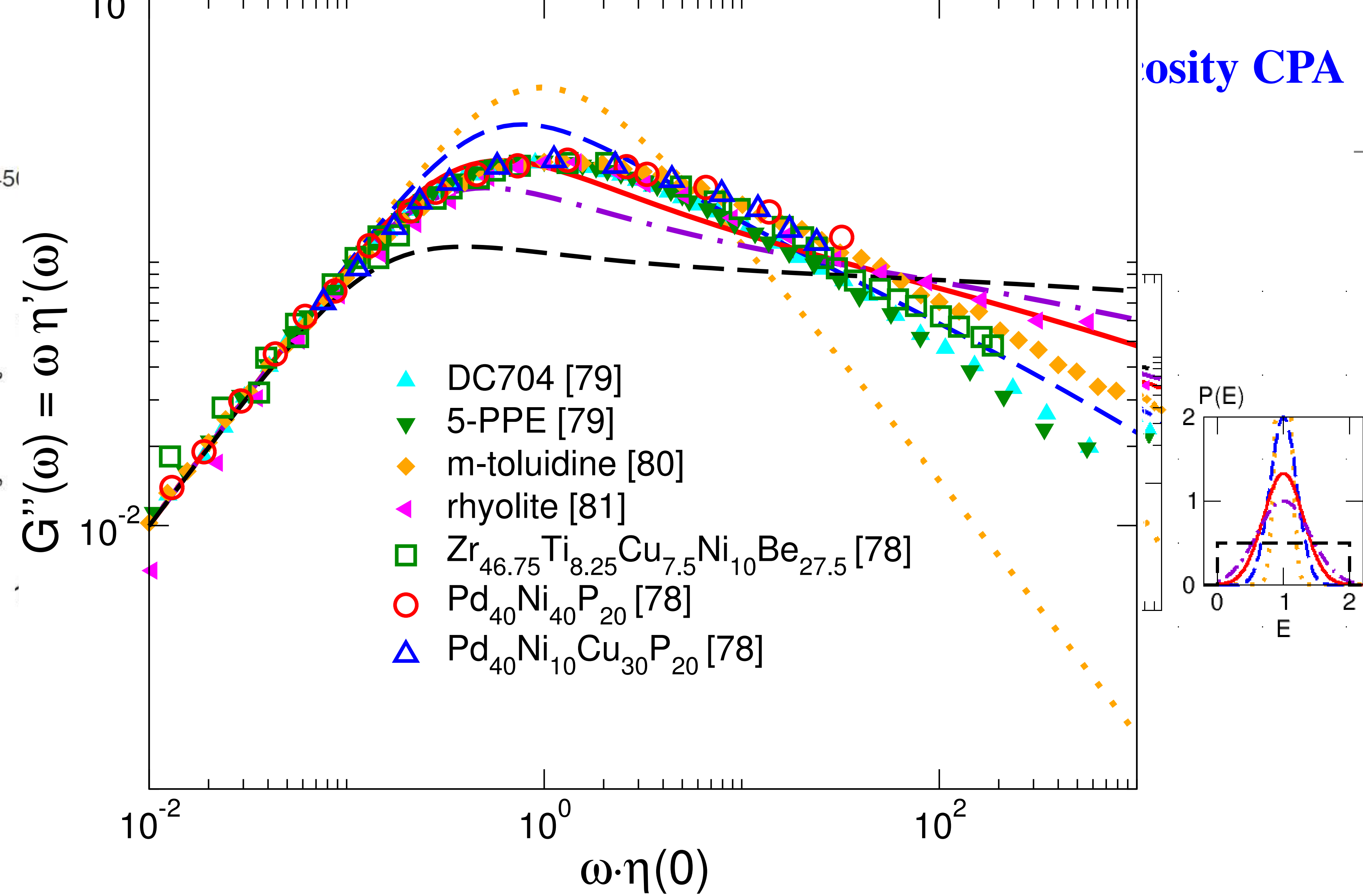
Wang et al. JCP 128,164503 (2008)



CPA calculation with varying σ

$$P(E) = P_0 e^{\frac{1}{2}(E-E_0)^2/\sigma^2}$$

osity CPA



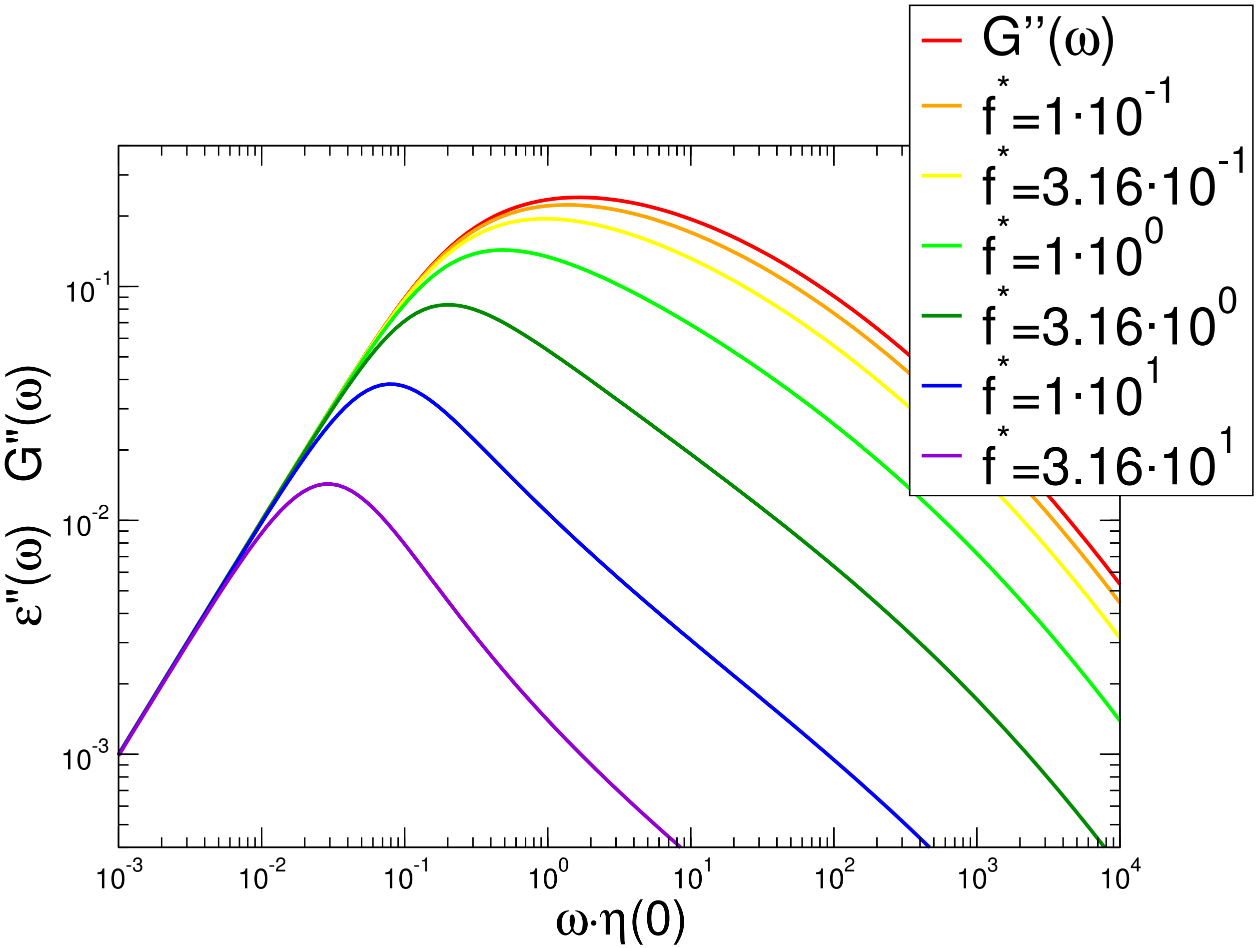
$$P(E) = P_0 e^{\frac{1}{2}(E-E_0)^2/\sigma^2} \qquad \text{———} \qquad \frac{\sigma}{E_0} = 0.3$$

W. Schirmacher et al., PRL 115, 015901 (2015)

Dielectric and mechanic loss functions in CPA

$$\epsilon''(\omega) \propto \mathrm{Im}\left\{\frac{1}{1+f^* G(\omega)}\right\}$$

Gemant-DiMarzio-Bishop equation, Niss et al. JCP 123, 234510 (2005)



High frequency limit: Heterogeneous elastic model

W. Schirmacher, EPL 2006, W.S. *et al.*, PRL 2007, Marruzzo *et al.* Nature Sci. Rep. 2013

- At very high frequency (much above the relaxation regime) the inhomogeneous-viscoelastic Navier-Stokes equations become equal to the inhomogeneous-elasticity equations.

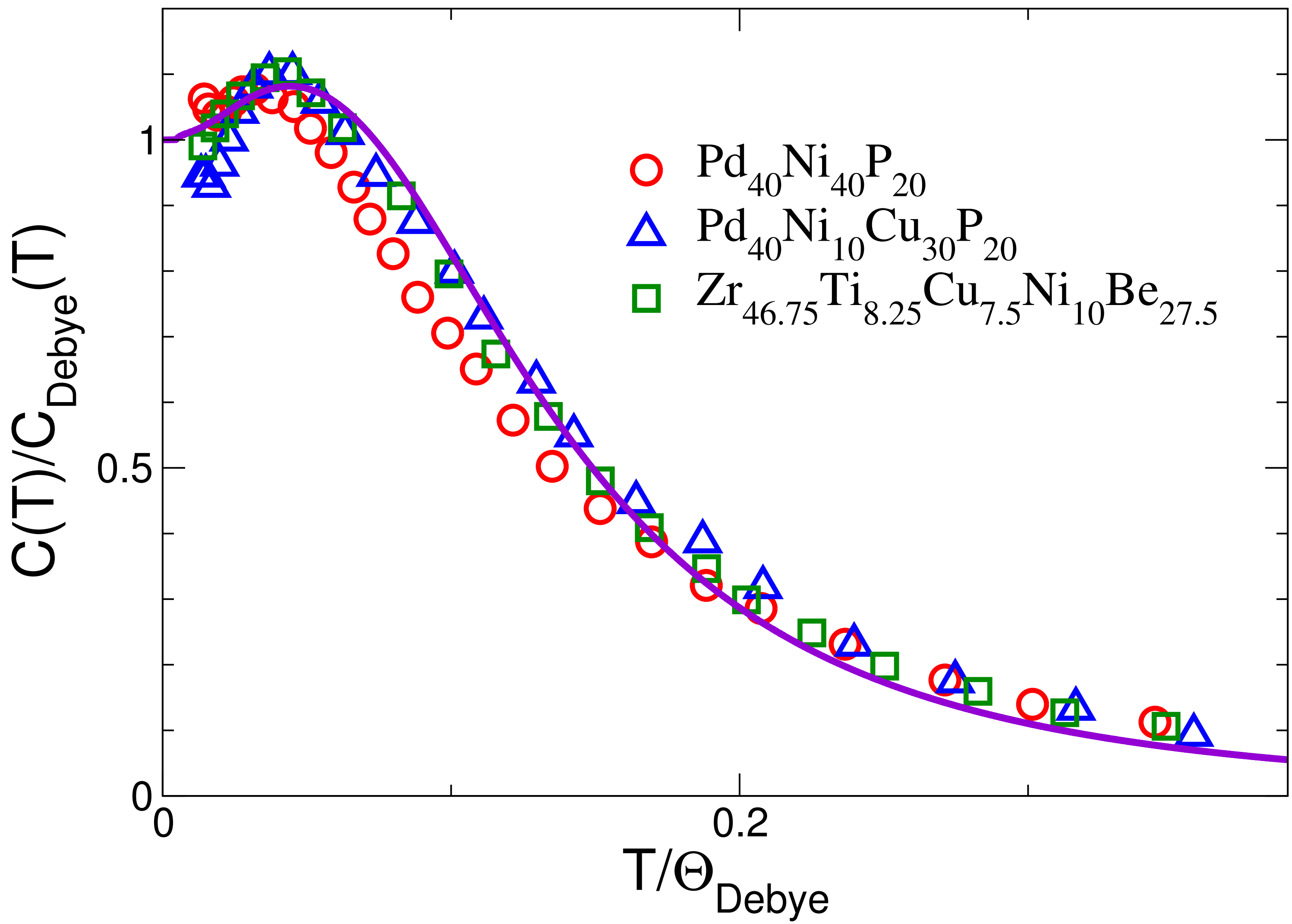
$$\rho_m(-\omega^2)u_i(\mathbf{r},\omega) = K\nabla^2 u_i + 2\sum_j \nabla_j G(\mathbf{r})\hat{\epsilon}_{ij}(\mathbf{r},\omega)$$

$$\epsilon_{ij} = \tfrac{1}{2}(\nabla_i u_j + \nabla_j u_i) \qquad \hat{\epsilon}_{ij} = \epsilon_{ij} - \tfrac{1}{3}\delta_{ij}\mathrm{Tr}\{\epsilon_{ij}\}$$

- This model, solved in self-consistent Born approximation (SCBA) or Coherent-potential approximation (CPA) is capable to explain the high-frequency vibrational anomalies in glasses (“boson peak”)

Specific heat of bulk metallic glasses

We compare the specific heat of the same metallic glasses as before with CPA calculatios using the same width-to-mean ratio $\sigma/E_0 = \sigma_G/G_0 = 0.3$, which fitted best the relaxation data.



Conclusions

- A heterogeneous visco-elastic theory has been worked out and solved in coherent-potential approximation (CPA)
- The viscosity is assumed to vary statistically in space.
- The theory is valid both for the frequency-dependent viscosity as well as for its $\omega \to 0$ limit.
- The alpha relaxation asymmetry is explained by the presence of the heterogeneous disorder together with a Gaussian distribution of activation energies
- At high frequencies the theories goes over to heterogeneous elasticity theory, which explains the boson-peak related vibrational anomalies.

Thank you for your attention