Understanding non-exponentiality and non-Arrhenius temperature dependence through memory functions

Nicholas Bailey

DNRF centre “Glass and Time,”
IMFUFA, Department of Sciences
Roskilde University

Fragility of Viscous Liquids: Cause(s) and Consequences
October 8–10, 2008

Correlation functions

- Typically we frame the big questions (of viscous liquid dynamics) in terms of correlation functions $\psi(t) \equiv \frac{\langle \Delta A(0) \Delta A(t) \rangle}{\langle (\Delta A(0))^2 \rangle}$
- Typical dynamical variables A: single-particle (molecular displacement/orientation/velocity, ...); "collective" (energy, pressure, shear stress, ...)
- Relaxation time is $\tau_\alpha \equiv \int_0^\infty \psi(t) dt = \tilde{\psi}(0)$ (ignore vibration)
- Experiments consider the same quantities in the frequency domain
- Why non-exponential relaxation? $[\psi(t) \sim exp(-(t/\tau_{KWW})^\beta)]$
- Why non-Arrhenius temperature dependence of relaxation times?

Is stretched exponential really a good description? Experiments suggest long time behavior is exponential.

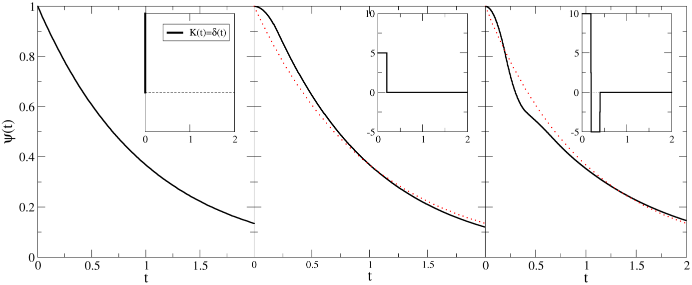
Memory function $\psi(t) \leftrightarrow K(t)$

- Memory function equation: $\frac{d\psi}{dt}(t) = -\int_0^t K(t-t')\psi(t')dt'$
- Laplace transform:
  $s\tilde{\psi}(s) - 1 = -\tilde{K}(s)\tilde{\psi}(s) \implies \tilde{\psi}(s) = 1/(s+\tilde{K}(s))$
- $s = 0$ gives $\int_0^\infty K(t)dt = \tilde{K}(0) = 1/\tilde{\psi}(0) = 1/\tau_\alpha$ ("$\int K$ is a rate")
- $K(t) \sim$ autocorrelation of the random changes ("noise") in generalized Langevin equation for the dynamical variable $A(t)$:

$$\frac{dA}{dt} = -\int_0^t K(t-t')A(t')dt' + \xi(t), \qquad \langle \xi(0)\xi(t)\rangle = k_B T K(t)$$

- $\xi(t) \leftrightarrow$ random changes in A associated with PEL transitions.

A few examples



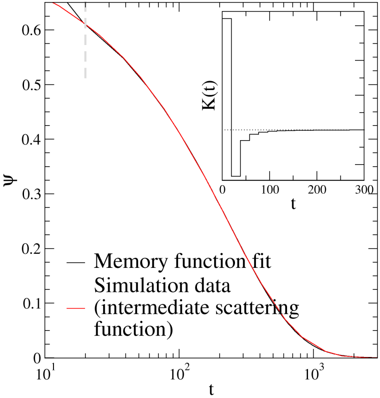
- $K = 0,\ t > T$, exponential at times $\gg t$, rate $\sim \int_0^T K$
- Generalizing intuitively: $\int_0^t K(t')dt' \sim$ effective rate at time t
- Negative $K(t) \rightarrow$ slower-than-exponential decay

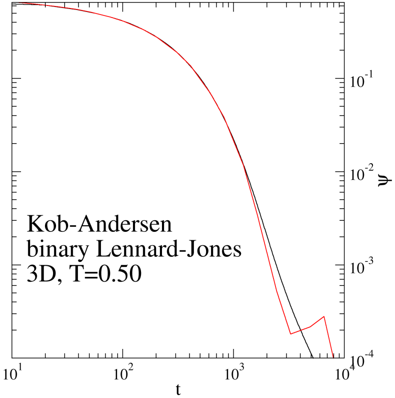
Practical details

- Discretized version $\psi_{n+1} - \psi_n = -\sum_{m=0}^{n} K_{n-m}\psi_m, \quad t_n = n\Delta t$
- K_0 covers the interval 0 to Δt, K_1 covers from Δt to $2\Delta t$, etc.
- Simplification when restricting to time scales greater than $\Delta t = 20$ (LJ units, $\sim$ 40 ps Argon)
- Choose a functional form for K_n and fit it to simulation $\psi(t)$
- Remove vibrational part of $\psi(t)$, make normalization factor $\langle(\Delta A)^2\rangle$ an independent fitting parameter

Negative inverse power-law accounts for almost everything

- $K_0 = (\psi_0 - \psi_1)/(\Delta t)^2 > 0$ (short-time rate, variance of changes in A)
- $K_n \propto -\frac{1}{t^\alpha} < 0$, $n > 0$ (anti-correlation of random changes in A)
- Self-ISF, autocorrelation functions of p, σ_{shear}, 2D, 3D

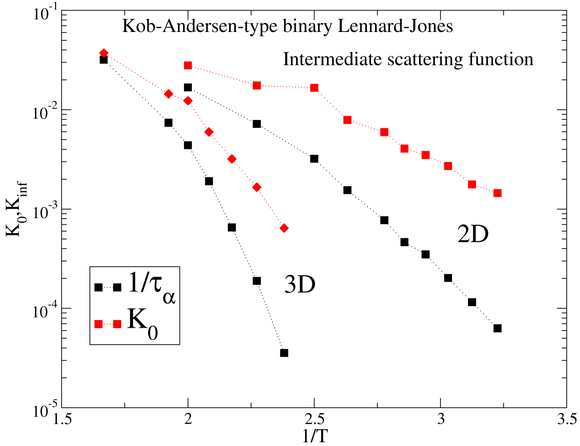




Interpretation (what do we get from this?)

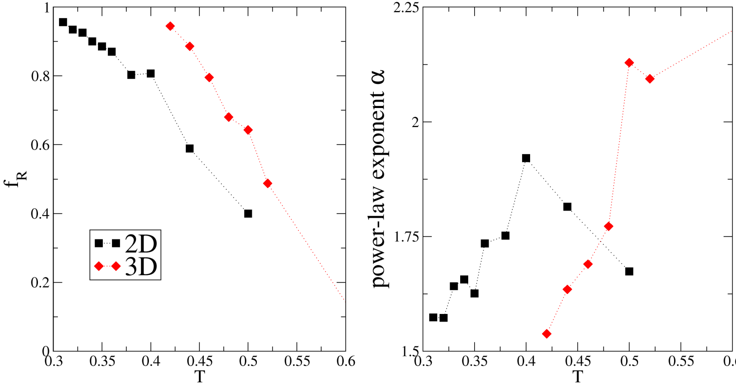
- First parameter: $K_0 \equiv (\psi(0) - \psi(\Delta t))/(\Delta t)^2$ ("t=20 relaxation rate")
- Second parameter: exponent α in negative inverse power law ("scale-free probability for reverse events")
- Third parameter: power-law amplitude, in terms of $f_R \equiv -(\sum_{n \geq 1} K_n)/K_0$ ("integrated return probability")
  - $f_R \rightarrow 0$ gives exponential decay for $t \gg \Delta t$
  - $f_R \rightarrow 1$ gives $\tau \rightarrow \infty$ (Cole-Cole, see later)
- Overall relaxation time $\tau_\alpha \propto \frac{1}{K_0} \frac{1}{1-f_R}$

Arrhenius or not?



- Underlying Arrhenius behavior? (cf. de Souza and Wales PRL 96, 057802 (2006) Arrhenius on timescales $\sim$ 25)

Reversal probability, $f_R = -\Sigma_{n>0} K_n / K_0$



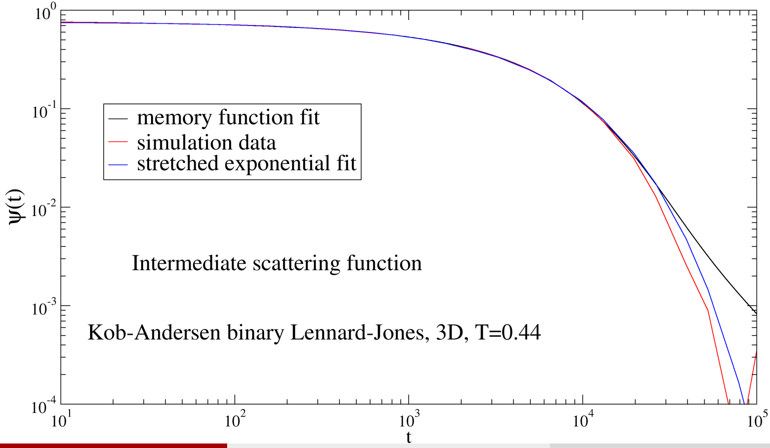
- Growth of f $\rightarrow$ non-Arrhenius and non-exponentiality
- What determines T-dependence of f_R, limiting value of α ($\sim 3/2$)?
- Connection with the potential energy landscape?

Is there something special about the $f_R \to 1$ limit?

- $f \to 1$ leads to $\tilde{K}(s) \to \tau_{CC}^{\alpha-2} s^{\alpha-1}$, $\tau_{CC} \sim (K_0(\Delta t)^\alpha)^{1/(\alpha-2)}$
- Correlation function $\psi(t) = E_\beta(-(t/\tau_{CC})^\beta)$, $\beta = 2 - \alpha$ (Mittag-Lefler function)
- $E_\beta(x) \sim \exp(x), \quad x \lesssim 1; \qquad E_\beta(x) \sim 1/x, \quad x \gg 1$
- Spectrum: $1 - s\tilde{\psi}(s) = 1 - \frac{s}{s+\tau_{CC}^{-\beta} s^{1-\beta}} = \frac{1}{1+(\tau_{CC} s)^\beta}$ (Cole-Cole)
- Anti-correlation between successive changes persists under coarse-graining in time
- $f_R \to 1$ limit is a fixed point in the renormalization group sense
- A starting point for understanding slow dynamics?
- Perhaps the beta process should not really be considered merely a "secondary process"?

Long time behavior

- Something else happening at longest times?
- Experiments: $\psi(t) \sim$ exponential at long times
- Can argue that same must hold for $K(t)$



Summary and next steps

Summary

- A way of analyzing correlation functions which
  - Isolates short-time relaxation rate (near Arrhenius)
  - Exhibits timescale-free behavior in the dynamics (anti-correlation of changes)
- Suggests reverse transitions more important than we think
- Suggests Cole-Cole process, normally associated with beta relaxation, might play a more fundamental role

Next steps

- Pin down T-dependence of α, f_R at low-T, long-τ_α
- Look at more fragile systems (e.g. OTP)
- Look at experimental data
- Try to understand scale-free behavior in simple models
- Find a physical mechanism for cutting off $K(t)$ at long times