Thermal Conductivity of a glass-forming liquid

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Outline

- Introduction
- Heat transport in the Kob-Andersen binary Lennard-Jones mixture

  Results from equilibrium and non-equilibrium simulations.

  Analysis of local energy minimas in the harmonic approximation.
- Discussion

Introduction

- A structural glass results when a liquid (composed of atoms/molecules) is cooled sufficiently quickly, and the glassy state is characterized by a freezing-in of local structures that prohibit easy movement of the particles, breaking the ergodicity of the system.

- A glass is something that does not thermalize/equilibrate. Inability to thermalize suggests that the system is a bad heat conductor. This is true for many experimental glassy systems — much lower values of κ than crystals.

- Thermal conductivity of glasses: some questions.

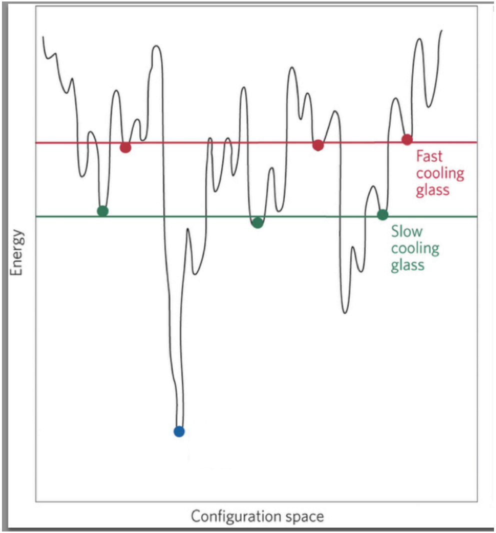
  - What is the temperature dependence of κ ? Are there any features of a transition when one measures κ across the "glass transition temperature" ?
  - Are there signatures of aging ? Does thermal conductivity change as you wait ?
  - At very low temperatures, the system is confined to one of the configurational minimas and can be described in the harmonic approximation (as a random harmonic network).

    Properties of the normal modes of the disordered solid (density of states, localization, diffusivity)

    Is κ finite ? Variation of κ between different minimas ?

    Can intermediate temperature behaviour be understood in terms of transitions between these minimas ?

Picture of the potential energy landscape



Experimental features: Plateau of thermal conductivity

Experimental data on specific heat and thermal conductivity of crystalline SiO_2 (Quartz) and amorphous SiO_2 — Boson peak in C and plateau in κ.

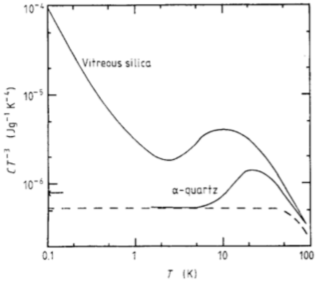


Figure 1. The heat capacity $C(T)$ of vitreous silica and crystalline quartz as a temperature T (Jones 1982, after Zeller and Pohl 1971), plotted as C/T^3 aga

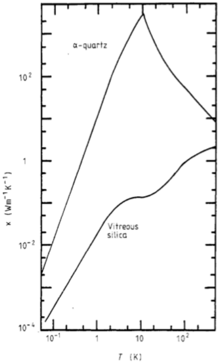


Figure 2. The thermal conductivity $\kappa(T)$ of vitreous silica and crystalline quartz (Jones 1982, after Zeller and Pohl 1971), plotted logarithmically.

A lot of work on trying to understand these features: mostly heuristic and phenomenological (focus on low temperature quantum effects).

Present work: thermal transport near the glass transition temperature

Earlier work - 1

- Elastic heterogeneity, vibrational states, and thermal conductivity across an amorphisation transition — H Mizuno, S Mossa, JL Barrat, EPL (2013)
- Lennard-Jones mixture is studied. Size ratio of particles is varied so one can go from crystalline state to glassy state.
- Look at thermal conductivity using Green-Kubo equilibrium simulations. Also look at density of states, localization and heterogenity in elastic properties.

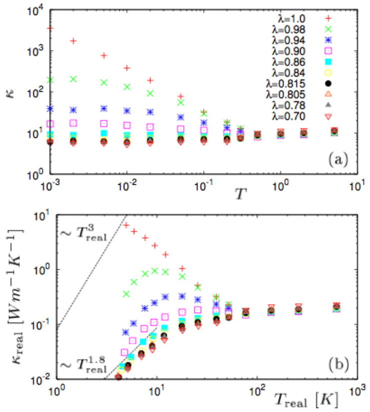


Fig. 6: The temperature dependence of thermal conductivity κ for $\lambda = 1$ to 0.7. (a) The values obtained from MD simulations and (b) the values with quantum corrections. In (b), T_{real} and κ_{real} are measured in units of K and $Wm^{-1}K^{-1}$, respectively.

Earlier work - 2

Thermal conductivity in the harmonic approximation.

$$\kappa = \int_0^{\omega_d} d\omega C(\omega) d(\omega) g(\omega)$$

- Heat transport in model jammed solids — Xu, Vitelli, Wyart, Liu, Nagel, PRL (2009), PRE (2010).
- Look at disordered harmonic networks obtained from minimum energy configurations of soft sphere packings very close to the jamming transition.
- Find normal modes. Compute density of states, diffusivity $d(\omega)$, localization.
- Main findings: difference between stressed and unstressed systems. Small fraction of localized modes.

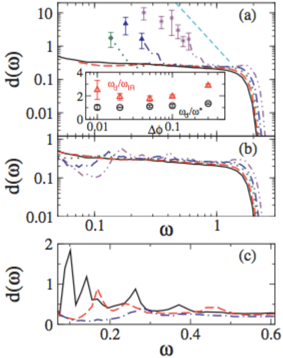
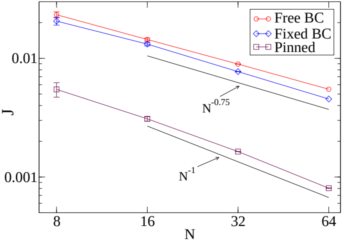


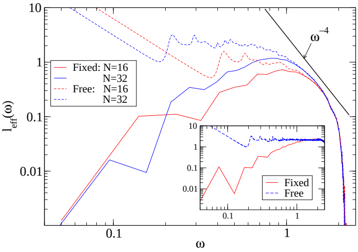
FIG. 2 (color online). Diffusivity versus compression. $d(\omega, \eta = 0.002, N = 2000)$ for the (a) unstressed and (b) stressed systems at $\Delta\phi = 10^{-6}$ (solid black line), 0.01 (red dashed line), 0.05 (green dotted line), 0.1 (blue dot-dashed line),

Earlier work - 3

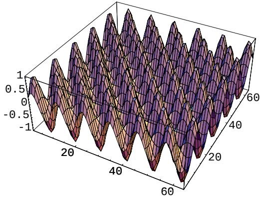
- Heat transport in mass-disordered harmonic crystals — Kundu, Chaudhuri, Dhar, Lebowitz and Spohn, PRB, EPL (2010).
- Look at particles with random masses on a cubic lattice. Look at transmission $T(\omega)$, diffusivity $d(\omega)$, density of states and localization. Also study system size dependence of conductivity.
- Main findings: Fourier law not valid in unpinned system $\kappa \sim L^{0.25}$. Finite κ for pinned crystal. Small fraction of localized modes. Anomalous transport due to low frequency sound modes.



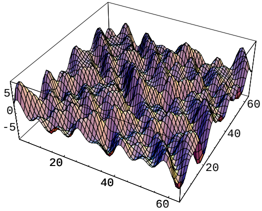
Diffusivity $d(\omega) = \ell(\omega)v$.



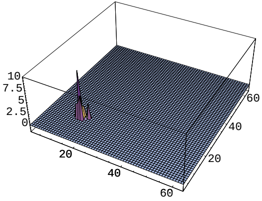
Character of normal modes of a disordered crystal



Extended periodic mode
(Ballistic)



Extended random mode
(Diffusive)



Localized mode
(Non-conducting)

Present work

A more detailed study of heat transport in a model glass former — A Lennard-Jones mixture

- Study heat transport in a model glass former — Kob-Andersen Glass.
- 80 : 20 A-type and B-type particles interacting via the Lennard-Jones pair potential,

$$V_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] .$$

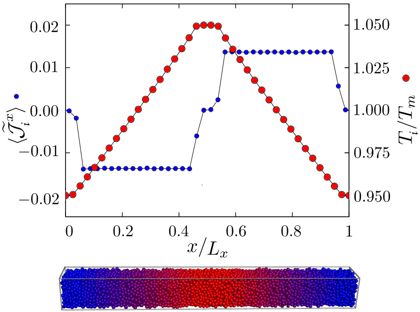
- Parameters: $\sigma_{AB} = 0.8\sigma_{AA}$, $\sigma_{BB} = 0.88\sigma_{AA}$, $\epsilon_{AB} = 1.5\epsilon_{AA}$, $\epsilon_{BB} = 0.5\epsilon_{AA}$.

  Set length, energy scales with $\sigma_{AA} = 1$ and $\epsilon_{AA} = 1$. Number density $\rho = 1.2$.
- Various "transition temperatures": $T_0 \approx 0.3$, $T_{MCT} \approx 0.435$

Methods

Three different methods to calculate thermal conductivity.

1. Non-equilibrium molecular dynamics simulations (NEMD)



2. Compute current-current autocorrelation from equilibrium simulation and use Green-Kubo formula.

$$\kappa = \frac{1}{3k_B T^2 V} \int_0^\infty dt \langle \mathbf{J}(0).\mathbf{J}(t) \rangle$$

3. At low temperature, assume harmonic approximation around local potential minimum. Compute conductivity from the eigenvalues and eigenvectors of Hessian matrix.

Simulation details

NEMD

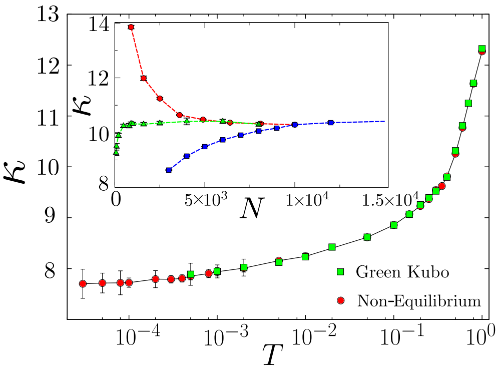
- Cooling protocol: Start from high temperature and go to lower temperatures in finite number of steps. Equilibriate system at each step at T for $t = 50 - 15000$ (depends on cooling rate).
- At each step, apply the gradient $\Delta T = 0.1T$ for $t = 25000 - 50000$. Obtain steady state averages over last $4/5$th of total run-time.
- Consider rectangular slab with $N = \rho \times L \times W^2$ particles at fixed density $\rho = 1.2$. Periodic boundary conditions.
- Look at $32 - 128$ independent runs. Small sample to sample fluctuations.

EMD

- Equilibrate at each T using NVT dynamics, then switch on NVE dynamics and compute current autocorrelation (averaging over both time and over initial conditions).
- Consider cubic box with $N = \rho \times L^3$ particles.

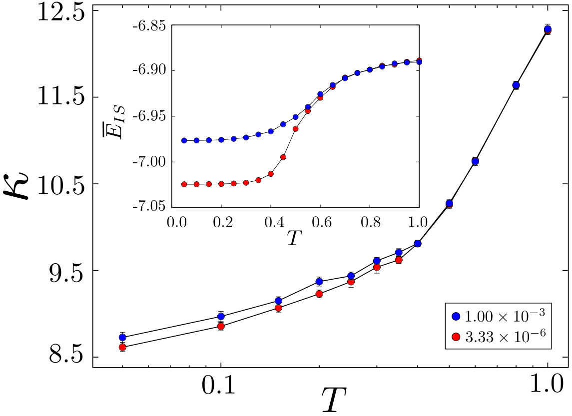
Numerical results

Results for thermal conductivity as a function of temperature — NEMD and Green-Kubo.
INSET — Finite size effects in NEMD (length and cross-section), and EMD (number of particles) NEMD: $N = \rho L W^2$; EMD: $N = \rho L^3$.



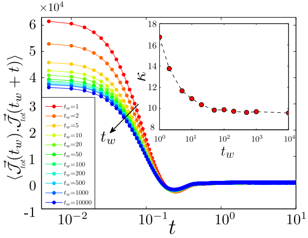
- κ from NEMD and EMD agree
- No drastic change near T_c.
- Well below T_c, κ does not become T-independent, as expected for a harmonic solid.

Dependence on cooling rate



Thermal conductivity κ from NEMD measurements for two cooling rates.

Dependence on cooling rate



Energy current autocorrelation function measured after different waiting times. Quenched from $T = 2.5$ to $T = 0.3$.

Compare with density relaxation (Kob and Barrat, 1997)

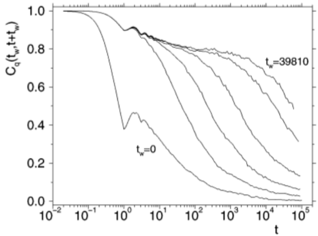
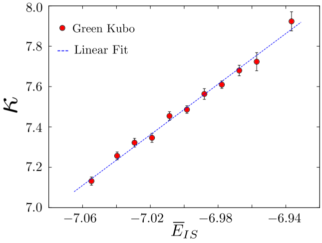


FIG. 2. $C_q(t_w, t + t_w)$ versus t for $t_w = 0$, 10, 100, 1000, 10 000, and 39 810 (from left to right); $T_i = 5.0$, $T_f = 0.4$, and $q = 7.2$.



κ obtained from EMD for different inherent energy structures. κ decreases linearly with E_{IS}.

Harmonic description

- Imagine the system moving in a $3N$-dimensional potential energy landscape (PEL). This PEL (temperature-independent) will have a large number of minimas.
- At high temperatures, the system is able to jump between minimas.
- At very low temperatures, we expect it to be trapped in a minima and perform small oscillations around the minima.
- Then system can be effectively descibed by expanding the potential around the minima:

$$V(\vec{r_i}) = V(\vec{r_{i,0}}) + \frac{1}{2} \sum_{i,j,\alpha,\beta} H_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \dots ,$$

to get the effective harmonic Hamiltonain

$$\mathcal{H} = \sum_i \frac{\vec{p_i}^2}{2m} + \frac{1}{2} \sum_{ij\alpha\beta} H_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta .$$

Allen-Feldman formula — Green-Kubo for a harmonic system

For a harmonic system, one can evaluate the equilibrium current autocorrelation function $\langle \mathbf{J}(0).\mathbf{J}(t) \rangle$ in terms of the normal modes eigenfunctions and eigenvalues:

$$\kappa = \int_0^\infty d\omega \; g(\omega) \; d(\omega) \; C(\omega)$$

$g(\omega) = (1/V) \sum_m \delta(\omega_m - \omega)$ — density of vibrational modes

$C(\omega) = k_B$ (for classical systems)

Phonon diffusivity given by

$$d(\omega) = \frac{\pi}{12 M^2 \omega^2} \int_0^\infty d\omega' g(\omega') \times \frac{(\omega + \omega')^2}{4\omega\omega'} |\vec{\Sigma}(\omega, \omega')|^2 \delta(\omega - \omega')$$

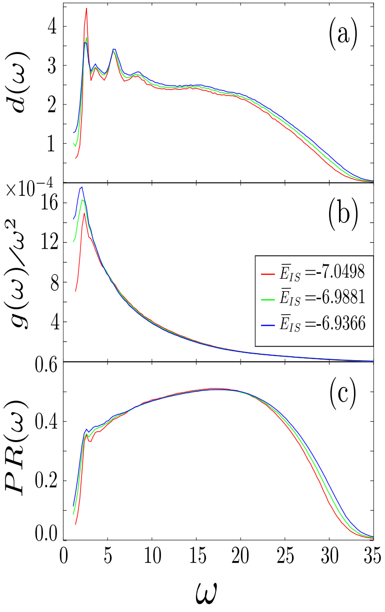
where the vector heat-flux matrix elements are

$$|\vec{\Sigma}(\omega, \omega')|^2 = \frac{\sum_{mn} |\vec{\Sigma}_{mn}|^2 \delta(\omega - \omega_m) \delta(\omega' - \omega_n)}{g(\omega) g(\omega')}$$

where m and n index the vibrational modes. The matrix elements $\vec{\Sigma}_{mn}$ can be computed from the hessian $H^{ij}_{\alpha\beta}$ and its m^{th} normalized eigenvector $e_m(i; \alpha)$

$$\vec{\Sigma}_{mn} = \sum_{i,j,\alpha,\beta} (\vec{r}_i - \vec{r}_j) e_m(i; \alpha) H^{ij}_{\alpha\beta} e_n(j; \beta) \; .$$

Harmonic limit: Numerical results



(a) Diffusivity

Note: diffusivity smaller for lower energy state at almost all frequencies.

(b) Density of states

Note: Boson peak shifts to lower frequncies with increasing IS energy.

(c) Participation ratio,

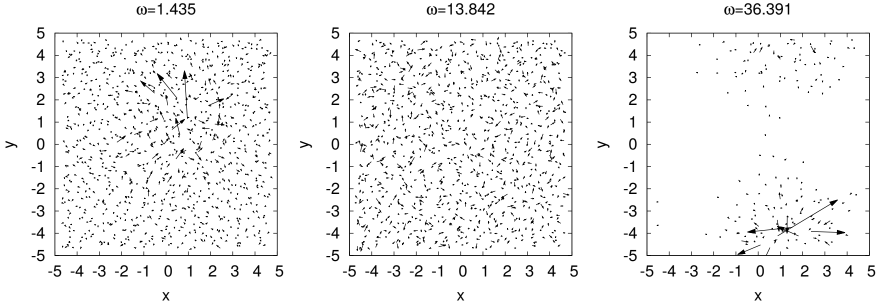
$PR(\omega_n) = [N \sum_\ell (\ \mathbf{e}_n(\ell).\mathbf{e}_n(\ell)\ )^2]^{-1}$.

Most states are delocalized.

Conclusion: lower energy inherent structures have lower conductivity because the associated normal modes are less extended and have smaller diffusivities (at almost all frequencies).

Nature of normal modes

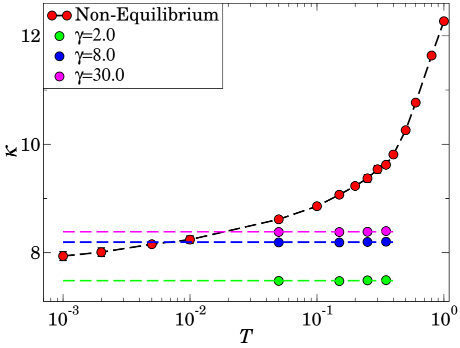
$N = 1000$, $E_{IS} = -7.036$
Projected normal modes for three different frequencies at the band edges and at the centre.



κ from the Allen-Feldman formula

Evaluating κ involves using regularized representations of δ-functions, with width γ.

For small systems, results for κ are sensitive to γ value — uncertainity in estimating κ.



Conclusions

- Thermal conduction does not show any dramatic changes near the transition point unlike relaxation times corresponding to viscosity.
- Clear signatures of ageing —

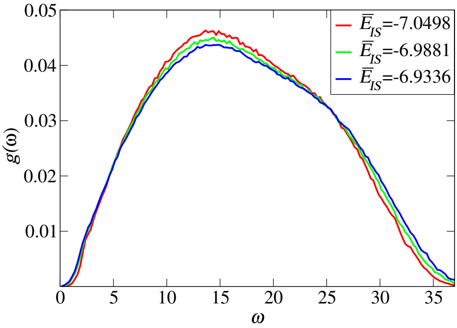
  $\kappa(T)$ depends on cooling rate.

  Close to the transition temperature, κ changes with waiting time.
- Dependence of thermal conductivity on cooling rates is related to exploration of lower energy minimas — lower energy minima have lower κ.
- Smaller κ related to lower diffusivity at all frequencies.
- Can a disordered harmonic system have a finite thermal conductivity ? [Ziman, Theory of solids].

  Apparently so for our glass, but need to go to larger sizes to confirm this — goldstone modes pushed to higher frequencies, lower frequencies quasi-localized (Lerner,During,Bouchbinder, 2016).

Details

Density of states



Details

Size dependence