Non-Equilibrium Thermodynamics of Glasses: The Kovacs Effect

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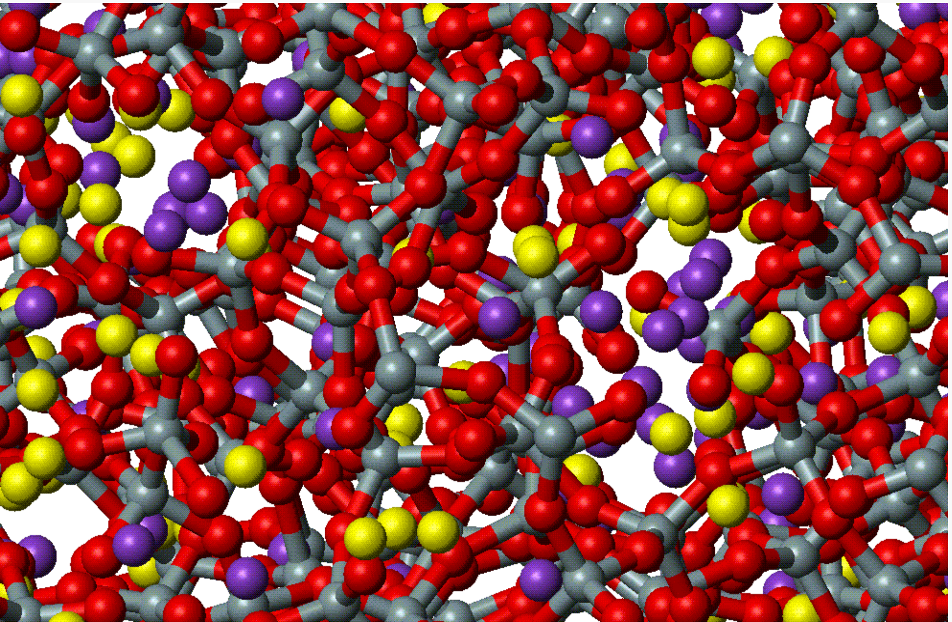
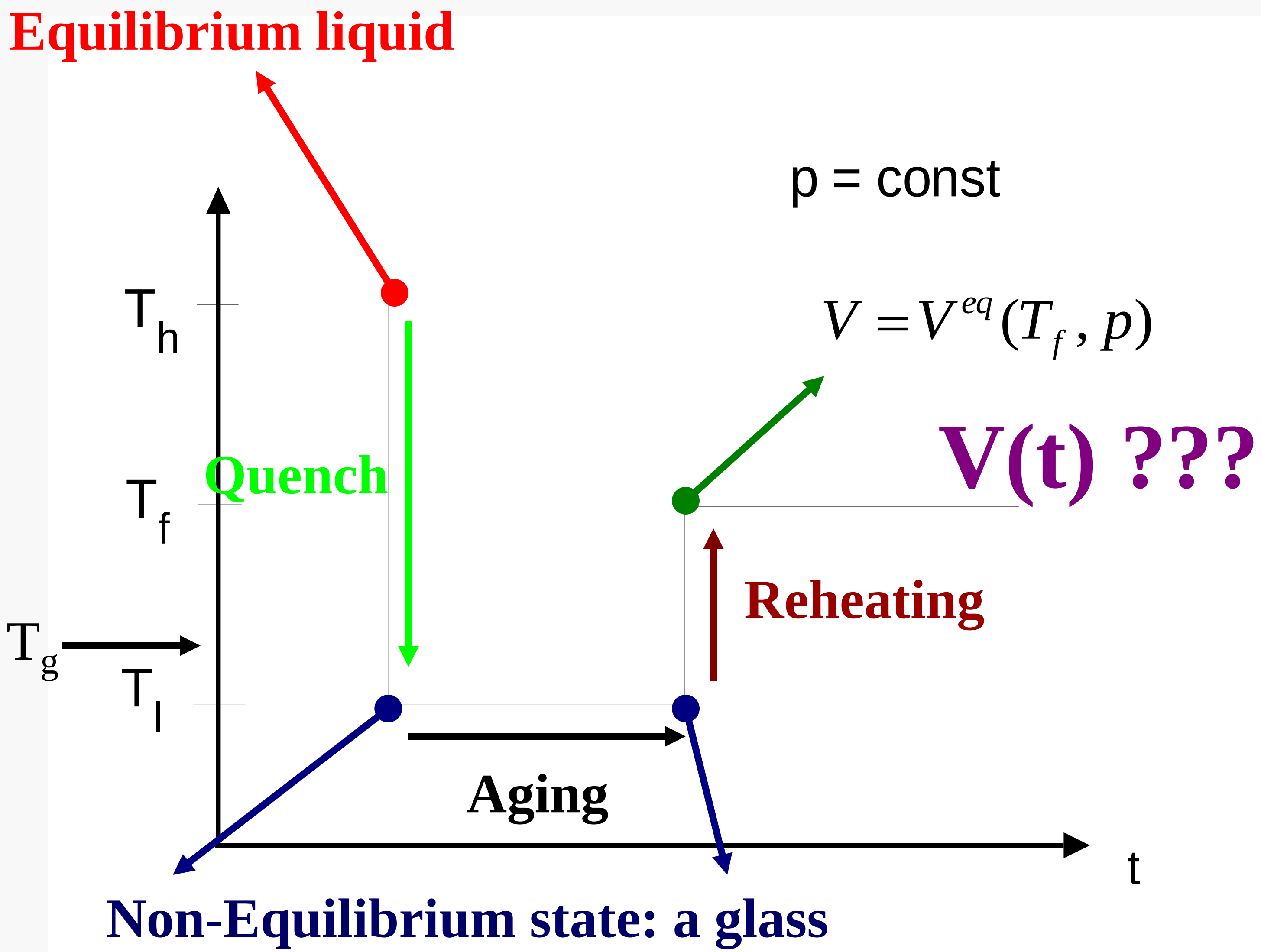


Work with James S. Langer
UC Santa Barbara

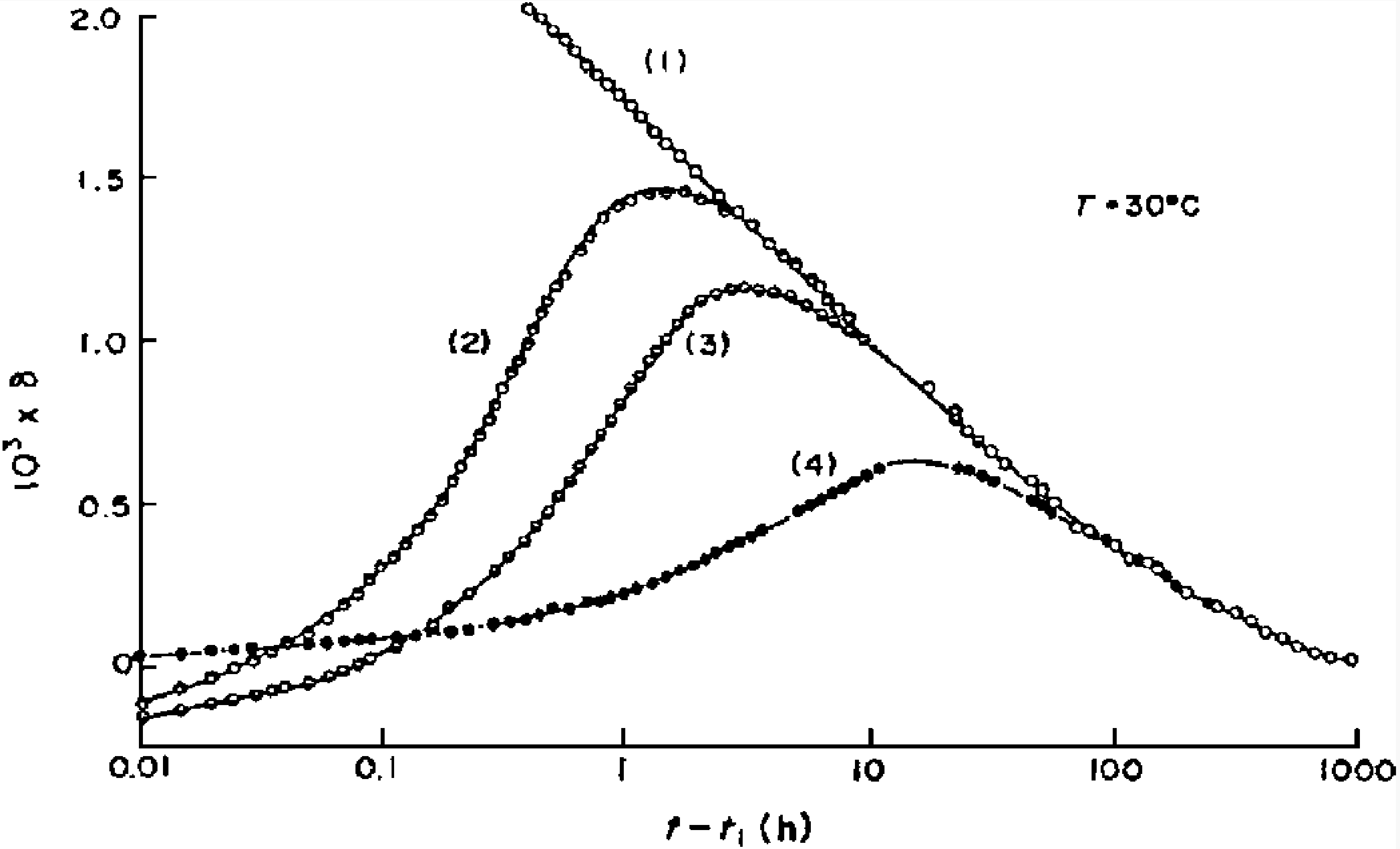
Statistical Mechanics Day
Weizmann, June 2010

The Kovacs Effect: A glassy puzzle



A. J. Kovacs, Adv. Polym. Sci. 3, 394 (1963)

Material: polyvinyl acetate (PVA, a glassy polymer)



- **The effect is generic and is observed in a variety of different glassy systems (e.g. colloidal glasses, ferroelectrics, gelatin gels, granular materials).**

- **Many specific models were shown to exhibit phenomena analogous to the Kovacs effect (e.g. coarsening dynamics in domain growth models, the trap model, the harmonic-oscillator–spherical-spin model).**

- **Main question:**

  Is there a generic non-equilibrium thermodynamic theory of the Kovacs effect?

Non-equilibrium thermodynamics of driven amorphous materials

Basic idea 1: Separable Configurational + Kinetic/Vibrational Subsystems

Total Energy $\simeq H_C + H_K$

$H_C = H_C\{r_\upsilon\}$ **= configurational energy of the ν'th inherent-structure**

$\{r_\upsilon\}$ **= set of molecular positions at the potential-energy minimum for the ν'th inherent-structure, SLOW dof**

$H_K = H_K\{p, \delta r_\upsilon\}$ **= kinetic energy + harmonic potential energy for small excursions from configurational minima, FAST dof**

Weak coupling between these two subsystems

EB & JS Langer, Physical Review E 80, 031131 (2009)
EB & JS Langer, Physical Review E 80, 031132 (2009)

Basic idea 2: The non-equilibrium state of the system can be characterized by coarse-grained internal variables

$$U_C(S_C, V_{el}, \{\Lambda_\alpha\}) \longleftrightarrow S_C(U_C, V_{el}, \{\Lambda_\alpha\})$$

The reversible part of the deformation

A subextensive number of coarse-grained internal variables, represent internal degrees of freedom that are coupled to deformation

Non-equilibrium entropy $S_C(U_C, V_{el}, \{\Lambda_\alpha\}) = \ln \Omega_C(U_C, V_{el}, \{\Lambda_\alpha\})$

A constrained measure of the number of configurations

When $\{\Lambda_\alpha\} \to \{\Lambda_\alpha^{eq}\}$ $\quad S_C(U_C, V_{el}, \{\Lambda_\alpha\}) \to S_C^{eq}(U_C, V)$

EB & JS Langer, Physical Review E 80, 031131 (2009)
EB & JS Langer, Physical Review E 80, 031132 (2009)

Basic idea 2 (cont.): The non-equilibrium state of the system can be characterized by coarse-grained internal variables

$$U_{tot} \simeq U_C(S_C, V_{el}, \{\Lambda_\alpha\}) + U_K(S_K, V_{el}) + U_R(S_R)$$

$$S_{tot} \simeq S_C(U_C, V_{el}, \{\Lambda_\alpha\}) + S_K(U_K, V_{el}) + S_R(U_R)$$

Temperatures

Vi

$$\chi = \left(\frac{\partial U_C}{\partial S_C}\right)_{V_{el},\{\Lambda_\alpha\}}, \quad \theta = \left(\frac{\partial U_K}{\partial S_K}\right)_{V_{el}}, \quad \theta_R = \frac{\partial U_R}{\partial S_R}$$

We'll assume

Reservoir

$$\theta = \theta_R$$

$$S_K = 3N\left[1 + \ln\left(\frac{U_K}{3N}\right)\right] - \sum_{n=1}^{3N} \ln(\omega_n)$$

Laws of Thermodynamics

1st Law: $-p\dot{V} = \dot{U}_{tot} = \dot{U}_C + \dot{U}_K + \dot{U}_R$

2nd Law: $\dot{S}_{tot} = \dot{S}_C + \dot{S}_K + \dot{S}_R \geq 0$

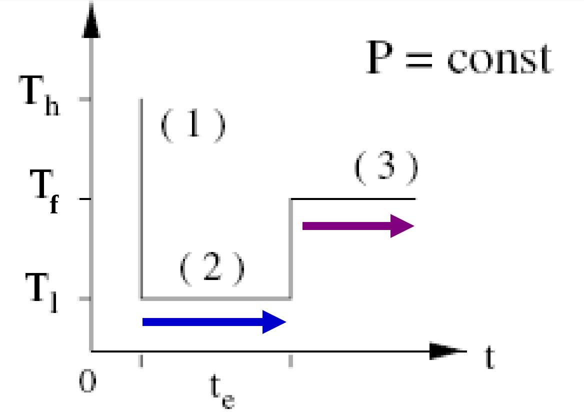
will be used to obtain EOM for: χ and $\{\Lambda_\alpha\}$

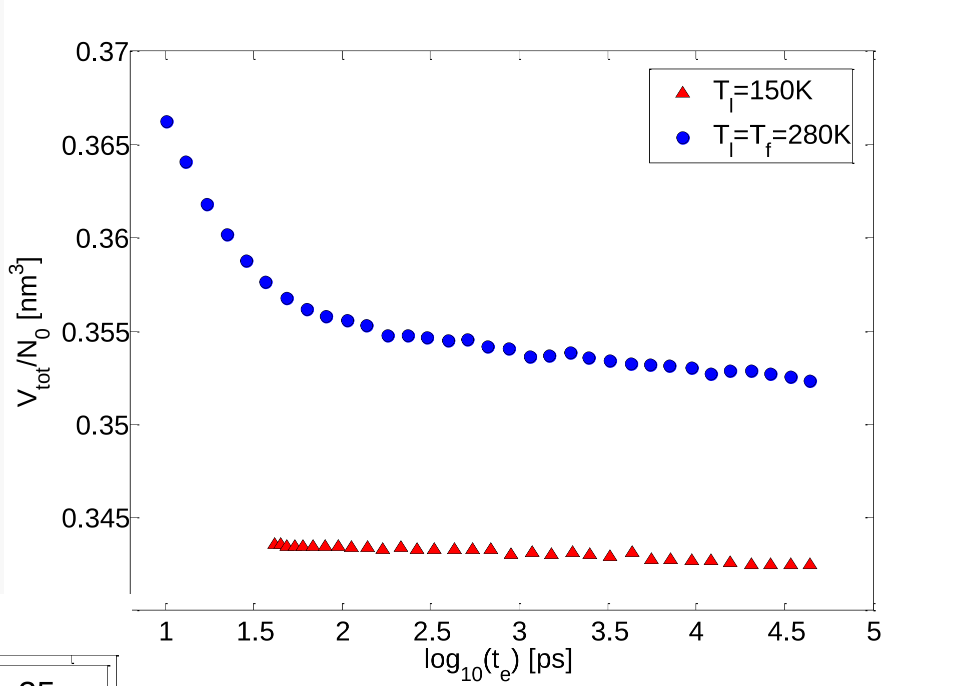
EB & JS Langer, Physical Review E 80, 031131 (2009)
EB & JS Langer, Physical Review E 80, 031132 (2009)

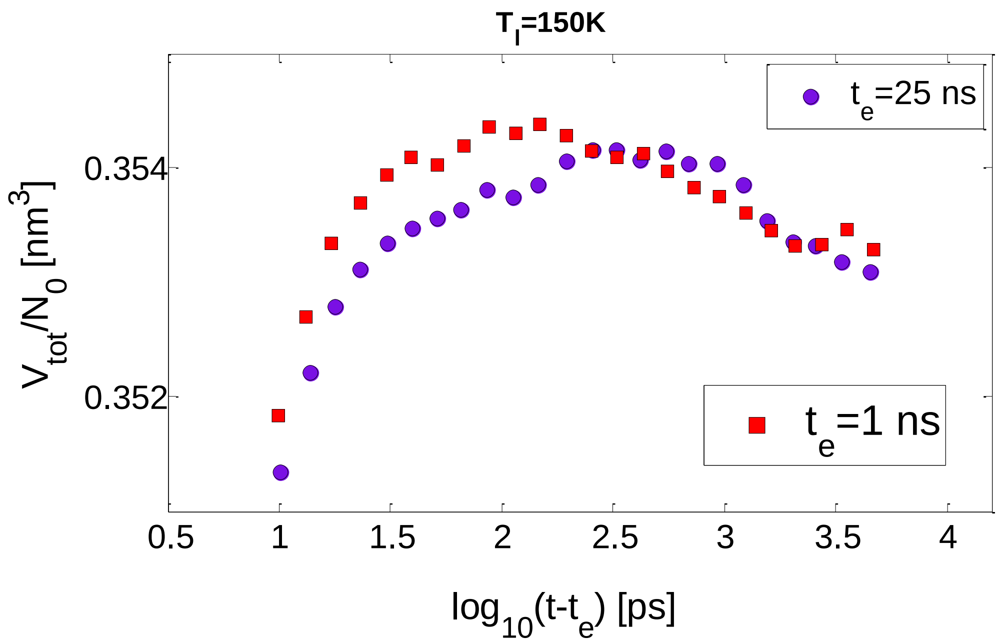
The Kovacs effect was recently observed in MD simulations of OTP

[S. Mossa and F. Sciortino, Phys. Rev. Lett. 92, 045504 (2004)]

$P=16MPa$, $T_h=400K$, $T_f=280K$,
$T_{MCT}=260K$, $T_m=330K$





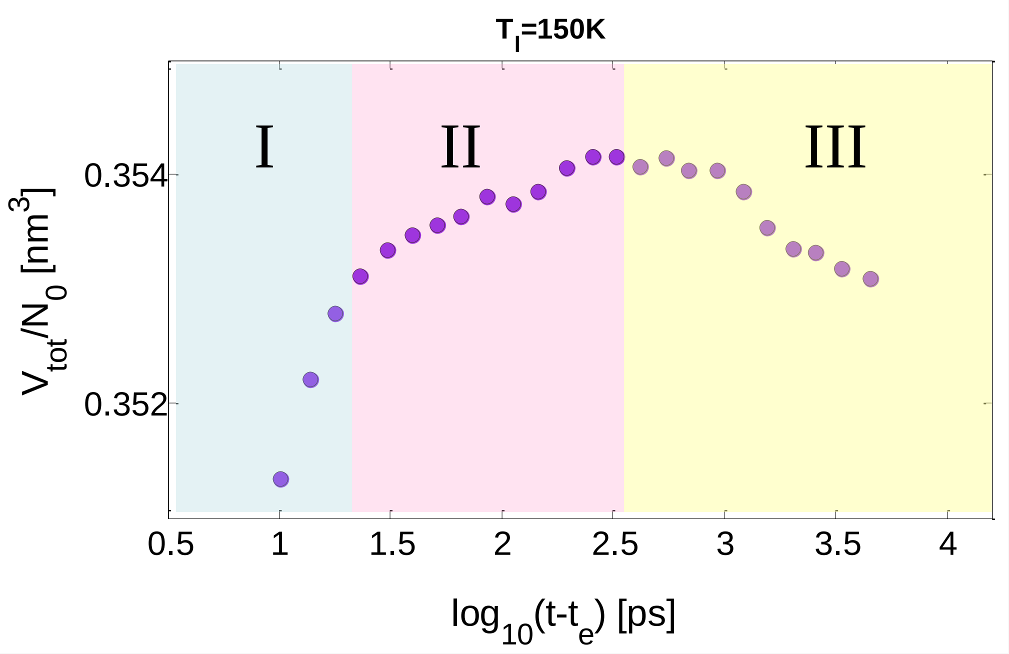


Thermal vibrations timescale:

$$\tau_0 \approx 1ps$$

Major new discoveries of the MD study

[S. Mossa and F. Sciortino, Phys. Rev. Lett. 92, 045504 (2004)]



Thermal vibrations timescale: $\tau_0 \approx 1ps$

Three stages:

I: Short timescales quenching effects

II: Intermediate timescales pre-peak dynamics

III: Long timescales post-peak aging

Major observation:

The dynamics in stage III follow a sequence of quasi-equilibrium states fully characterized by an effective temperature, while stage II cannot be described by an effective temperature alone.

A hierarchy of different non-equilibrium behaviors!

A Thermodynamic Theory of the Kovacs Effect

Two steps:

Step 1 – Identify internal state variables and associate with them energy and entropy

N_v - vacancy-like "defects" N_a - "misalignment defects"

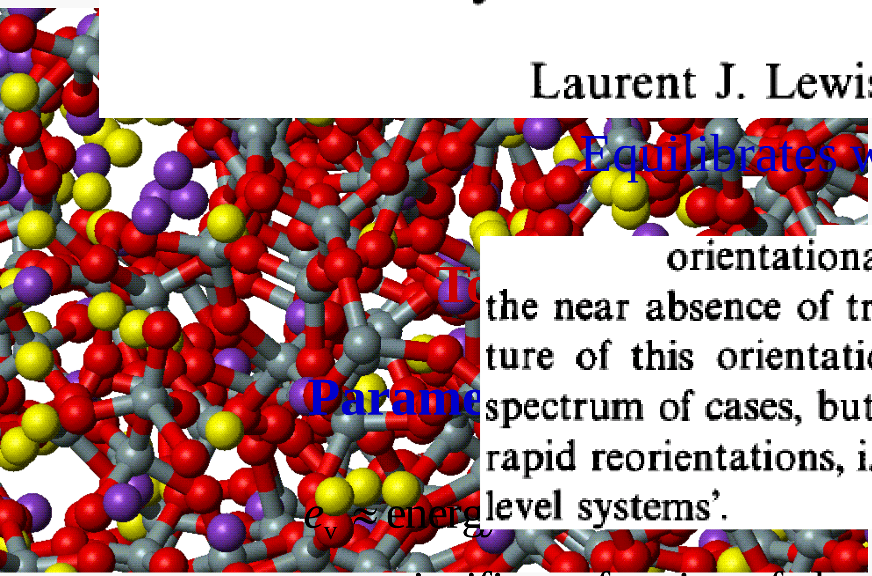
Step 2 – Derive equations of motion based on the laws of thermodynamics

Energy and excess volume e_v and v_v Energy and excess volume e_a and v_a

Journal of Non-Crystalline Solids 172–174 (1994) 69–76

Rotational dynamics in *ortho*-terphenyl: a microscopic view

Laurent J. Lewis*[,a], Göran Wahnström[b]



Equilibrates with χ Equilibrates with θ

orientational motion takes place despite the near absence of translational motion. The nature of this orientational motion covers a large spectrum of cases, but we find a preponderance of rapid reorientations, i.e., jumps or 'two- (or more-) level systems'.

$N_a \, v_a$

$e_v \approx$ energ

$v_v \approx$ significant fraction of the volume per molecule $\rightarrow 0.07\text{nm}^3, \quad v_a = 0.1 v_v$

EB & JS Langer, to appear in Soft Matter (2010)

A Thermodynamic Theory of the Kovacs Effect (cont.)

Step 2 – Derive equations of motion based on the laws of thermodynamics

2nd law:

$$
-\left[p\,v_a + \left(\frac{\partial U_K}{\partial N_a}\right)_{S_K,V_{el}}\right]\dot N_a
-\left[p\,v_0 + \left(\frac{\partial U_C}{\partial N_v}\right)_{S_C,V_{el}}\right]\dot N_v
-\Big[p - p_C(\chi,V_{el}) - p_K(\theta,V_{el})\Big]\dot V_{el} - (\theta-\chi)\,\dot S_K \geq 0.
$$

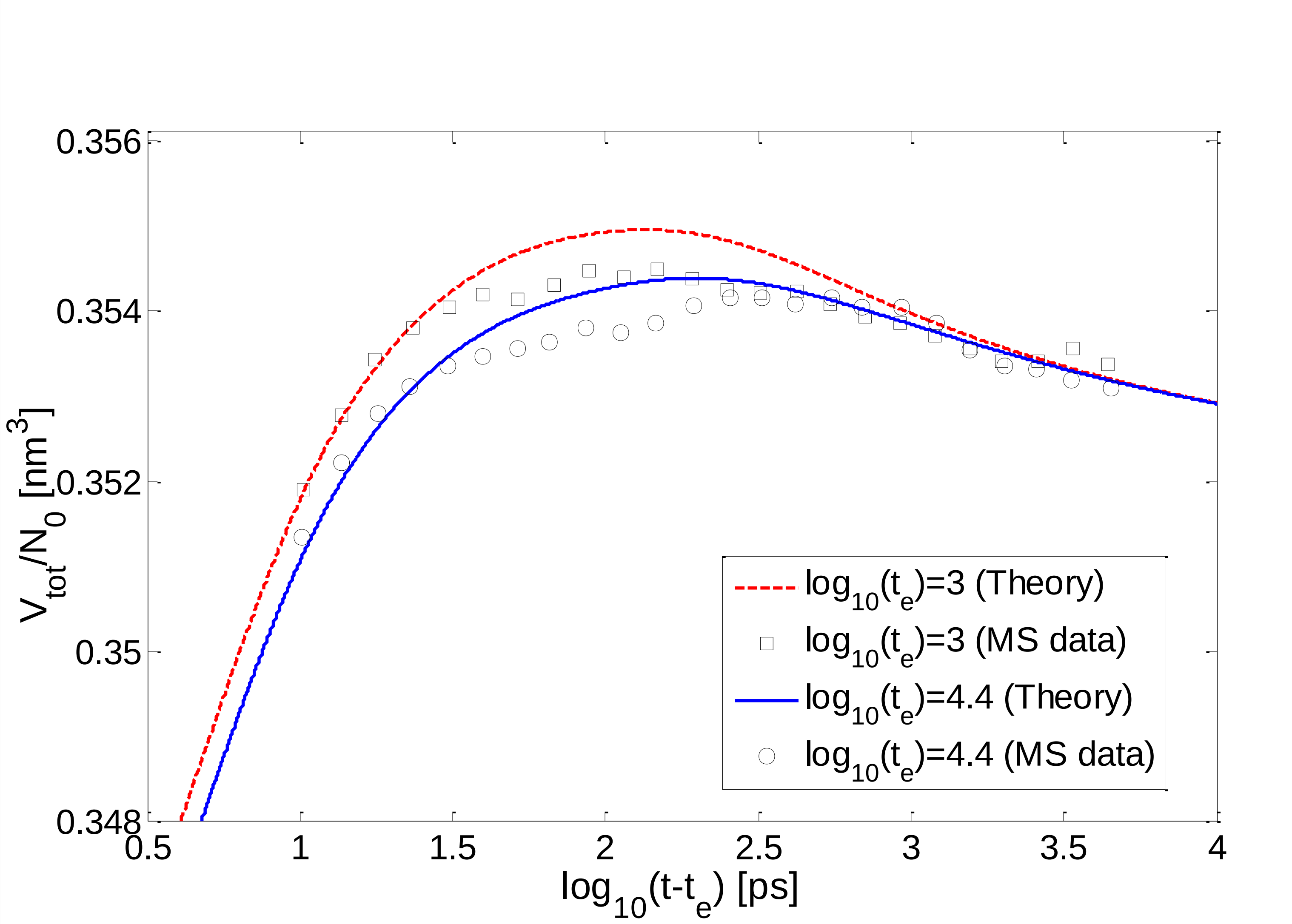
→ **4 independent inequalities**

1st law:

$$
\chi\,\dot S_C = -\left[h_v - \chi\,\frac{\partial S_0(N_v)}{\partial N_v}\right]\dot N_v - \left[h_a - \theta\,\frac{\partial S_0(N_a)}{\partial N_a}\right]\dot N_a
+ \frac{\gamma\,\bar\lambda}{V_0}\left[V_{el} - V_{el}^{eq}(\chi,\theta,p)\right]^2 + A(\chi,\theta)\left(1-\frac{\chi}{\theta}\right).
$$

EB & JS Langer, Soft Matter (2010)

Results



0.356
0.354
0.352
0.35
0.348
0.5
1
1.5
2
2.5
3
3.5
4
V_{tot}/N_0 [nm^3]
$log_{10}(t-t_e)$ [ps]
$log_{10}(t_e)$=3 (Theory)
$log_{10}(t_e)$=3 (MS data)
$log_{10}(t_e)$=4.4 (Theory)
$log_{10}(t_e)$=4.4 (MS data)

Conclusions

The Kovacs effect can be described within a non-equilibrium thermodynamics framework

A hierarchy of non-equilibrium processes are at play:

1) **A short time visco-elastic response (unique to extreme quenching rates)**

2) **Intermediate timescales processes:**

   An internal variable (n_a) that goes in and out of equilibrium directly with the heat bath

   An internal variable (n_v) that goes in and out of equilibrium with the effective disorder temperature

3) **Long timescales structural relaxation in which the effective temperature equilibrates with the heat bath (quasi-equilibrium)**